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**STUDIES ON ATOM TRANSFER RADICAL
POLYMERIZATION OF ACRYLATES AND
STYRENES WITH CONTROLLED POLYMERIC
BLOCK STRUCTURES**

Doctoral Dissertation

Khalid Ibrahim



**Helsinki University of Technology
Department of Chemical Technology
Laboratory of Polymer Technology**

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Department of Chemical Technology
Laboratory of Polymer Technology**

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Abstract <p>Atom transfer radical polymerization (ATRP) was applied to homo and block copolymerization of vinyl monomers methacrylates, acrylates, and styrene with iron ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$) as the transition metal in most cases. As complexing ligand either a commercially available ligand (triphenyl phosphine) (PPh_3) or synthetic aliphatic amines were used. As initiators, methyl 2-bromopropionate, ethyl 2-bromoisobutyrate, α, α-dichloroacetophenone, and poly(ethylene oxide) macroinitiator were employed. Block copolymerization of <i>n</i>-butyl methacrylate-<i>b</i>-<i>tert</i>-butyl acrylate (BMA-<i>b</i>-<i>t</i>BA) was performed by two-step ATRP method. The results showed that, for well-defined copolymers, a low conversion macroinitiator (conversion 35%) is preferable to a high conversion one.</p> <p>Four tetradentate nitrogen ligands, <i>viz.</i> dichloro{[<i>N,N'</i>-diphenyl-<i>N,N'</i>-di(quinoline-2-methyl)]-1,2-ethylene diamine} (1), {[<i>N,N'</i>-dioctyl-<i>N,N'</i>-di(quinoline-2-methyl)]-1,2-ethylene diamine} (2), {[<i>N,N'</i>-dibenzyl-<i>N,N'</i>-di(quinoline-2-methyl)]-1,2-ethylene diamine} (3), and (1<i>R</i>,2<i>R</i>)-(-)-<i>N,N'</i>-di(quinoline-2-methyl)diiminocyclohexane (4), were synthesised at the University of Helsinki, and used as complexing ligands in iron-mediated polymerization of methyl methacrylate. High to moderate conversions (87%, 43%) were obtained in relatively short times (90 min for 1 and 30 min for 2), which indicates an efficient catalyst system. When the bulkiness of the substituents was significantly increased, as in ligand 3, polymerization rate was decreased and control was lost. Ligand 4 was less efficient than the other ligands, probably because the ethylene bridge was replaced by cyclohexane bridge.</p> <p>Poly(ethylene oxide) monochloro macroinitiators and poly(ethylene oxide) telechelic macroinitiators (Cl-PEO-Cl) were prepared from monohydroxy functional and dihydroxy functional poly(ethylene oxide) in the presence of 2-chloro propionyl chloride and applied to the polymerization of styrene (S) or methyl methacrylate (MMA). The polymerization of styrene was carried out in bulk at 140 °C and catalysed by copper(I) chloride (CuCl) in the presence of 2,2'-bipyridine (bipy) ligand (CuCl/ bipy), but the polymerization of MMA was carried out in the presence of ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$)/ ($\text{PPh}_3$) catalytic system. With most of the macroinitiators, the living nature of the polymerizations led to block copolymers with narrow molecular weight distribution ($M_w/M_n < 1.3$). Adjustment of the content of the PEO blocks (>90% by mass) allowed the preparation of water-soluble/water-dispersible block copolymers. Small amounts of the PEO-PS-based block copolymers were applied to modify the paper surface. Chain length of the hydrophilic block and/or the amount of hydrophobic block was found to play an important role in modification of the paper surface. It was also found that water-dispersible triblock copolymer containing 10 wt-% PS makes the paper surface highly hydrophobic (contact angle $>115^\circ$) and retards water absorption on both light weight coated base paper (LWC) and fine base paper (FP). The effect on oil absorption was less significant.</p>							
Keywords		atom transfer radical polymerization, catalyst, controlled, macroinitiator, coating, paper surface					
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ABSTRACT

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Block copolymerization of *n*-butyl methacrylate-*b*-*tert*-butyl acrylate (BMA-*b*-*t*BA) was performed by two-step ATRP method. The results showed that, for well-defined copolymers, a low conversion macroinitiator (conversion 35%) is preferable to a high conversion one.

Four tetradentate nitrogen ligands, *viz.* dichloro{[*N,N'*-diphenyl-*N,N'*-di(quinoline-2-methyl)]-1,2-ethylene diamine} (**1**), {[*N,N'*-dioctyl-*N,N'*-di(quinoline-2-methyl)]-1,2-ethylene diamine} (**2**), {[*N,N'*-dibenzyl-*N,N'*-di(quinoline-2-methyl)]-1,2-ethylene diamine} (**3**), and (1*R*,2*R*)-(-)-*N,N'*-di(quinoline-2-methyl)diiminocyclohexane (**4**), were synthesised at the University of Helsinki, and used as complexing ligands in iron-mediated polymerization of methyl methacrylate. High to moderate conversions (87%, 43%) were obtained in relatively short times (90 min for **1** and 30 min for **2**), which indicates an efficient catalyst system. When the bulkiness of the substituents was significantly increased, as in ligand **3**, polymerization rate was decreased and control was lost. Ligand **4** was less efficient than the other ligands, probably because the ethylene bridge was replaced by cyclohexane bridge.

Poly(ethylene oxide) monochloro macroinitiators and poly(ethylene oxide) telechelic macroinitiators (Cl-PEO-Cl) were prepared from monohydroxy functional and dihydroxy functional poly(ethylene oxide) in the presence of 2-chloro propionyl chloride and applied to the polymerization of styrene (S) or methyl methacrylate (MMA). The polymerization of styrene was carried out in bulk at 140 °C and catalysed by copper(I) chloride (CuCl) in the presence of 2,2'-bipyridine (bipy) ligand (CuCl/bipy), but the polymerization of MMA was carried out in the presence of ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$)/ (PPh_3) catalytic system. With most of the macroinitiators, the living nature of the polymerizations led to block copolymers with narrow molecular weight distribution ($M_w/M_n < 1.3$). Adjustment of the content of the PEO blocks (>90% by mass) allowed the preparation of water-soluble/water-dispersible block copolymers. Small amounts of the PEO-PS-based block copolymers were applied to modify the paper surface. Chain length of the hydrophilic block and/or the amount of hydrophobic block was found to play an important role in modification of the paper surface. It was also found that water-dispersible triblock copolymer containing 10 wt-% PS makes the paper surface highly hydrophobic (contact angle $>115^\circ$) and retards water absorption on both light weight coated base paper (LWC) and fine base paper (FP). The effect on oil absorption was less significant.

PREFACE

This work was carried out in the Laboratory of Polymer Technology, Helsinki University of Technology, between 2002 and 2006. Parts of the work were funded by the Academy of Finland and other parts by the Finish Funding Agency for Technology and Innovation (TEKES).

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I owe a debt of great gratitude to my mother for her unwavering support throughout my life. She has been behind me at every moment, even when I didn't know where I was headed. She helped to show me where I should always find my direction. I can only hope to show the same kind of dedication and love to her.

Where would I be without my wife. She has made this experience and all the others in my life something worth doing.

A song of praise goes out to the Lord my God who is my source and has provided me with a community of good people who have made my life here both enjoyable and worthwhile. I know that without Him there is nothing I can do.

Espoo, June 1, 2006.

Khalid Ibrahim

LIST OF PUBLICATIONS

This thesis is based on the following five appended publications (Appendices I-V):

- I. Ibrahim, K., Löfgren, B., and Seppälä, J., Towards more controlled poly(n-butyl methacrylate) by atom transfer radical polymerization, *Eur. Polym. J.* **39**, 939–944 (2003).
- II. Ibrahim, K., Löfgren, B., and Seppälä, J., Synthesis of tertiary-butyl acrylate polymers and preparation of diblock copolymers using atom transfer radical polymerization, *Eur. Polym. J.* **39**, 2005–2010 (2003).
- III. Ibrahim, K., Yliheikkilä, K., Abu-Surrah, A., Löfgren, B., Lappalainen, K., Leskelä, M., Repo, T., and Seppälä, J., Polymerization of methyl methacrylate in the presence of iron(II) complex with tetradentate nitrogen ligands under conditions of atom transfer radical polymerization, *Eur. Polym. J.* **40**, 1095–1104 (2004).
- IV. Ibrahim, K., Starck, P., Löfgren, B., and Seppälä, J., Synthesis and characterization of amphiphilic triblock copolymers by iron-mediated atom transfer radical polymerization, *J. Polym. Sci., Part A: Polym. Chem.* **43**, 5049–5061 (2005).
- V. Ibrahim, K., Salminen, A., Holappa, S., Kataja, K., Lampinen, H., Löfgren, B., Laine, J., and Seppälä, J., Preparation and characterization of polystyrene-poly(ethylene oxide) amphiphilic block copolymers via ATRP: potential application as paper coating materials, *J. Appl. Polym. Sci.*, Accepted.

The author's contribution to the appended publications:

Publications I and II: I drew up the research plan, carried out the experimental work, interpreted the results, and wrote the manuscript.

Publication III: I drew up the research plan, carried out the polymerizations, interpreted the results, and wrote the manuscript. Aliphatic amine ligands and the corresponding complexes were synthesised and characterized by Katariina Yliheikkilä and Kristian Lappalainen in the Laboratory of Inorganic Chemistry, University of Helsinki.

Publication IV: I drew up the research plan and prepared the polymers. Thermal analyses (DSC and DMA) were carried out by Dr. Paul Starck in the Laboratory of Polymer Technology, Helsinki University of Technology, Dr. Starck also assisted in the interpretation of the results and writing of the manuscript.

Publication V: I drew up the research plan and prepared and characterized the polymers. The study on model surfaces and the written account of this part were done by Susanna Holappa, in the Laboratory of Forest Products Chemistry, Helsinki University of

Technology. Contact angle and polarity measurements were done by Kirsi Kataja, VTT Processes. Water and oil absorption measurements were carried out by Henna Lampinen, VTT Processes and felt-pen tests were done by Arto Salminen in the Laboratory of Polymer Technology, Helsinki University of Technology.

Other relevant publications

Yliheikkilä, K., Lappalainen, K., Castro, P., Ibrahim, K., Abu-Surrah, A., Leskelä, M., and Repo, T., Polymerization of acrylate monomers with MAO activated iron(II) and cobalt(II) complexes bearing tri- and tetradentate nitrogen ligands, *Eur. Polym. J.* **42**, 92–100 (2006).

STUDIES ON ATOM TRANSFER RADICAL POLYMERIZATION OF ACRYLATES AND STYRENES WITH CONTROLLED POLYMERIC BLOCK STRUCTURES

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ABBREVIATIONS

ATRP	atom transfer radical polymerization
BPC	2-bromopropionyl chloride
DSC	differential scanning calorimetry
DAMP	4-(dimethylamino) pyridine
DMA	dynamic mechanical analysis
FP	fine paper
FT-IR	Fourier transform infrared spectroscopy
GPC	gel permeation chromatography
LWC	light weight coated paper
MPEG	monohydroxyl poly(ethylene glycol)
M	monomer
NMP	nitroxide-mediated polymerization
PEG	poly(ethylene glycol)
PBMA-b- <i>Pt</i> BA	poly(butyl methacrylate)-block-poly(<i>tert</i> -butyl acrylate)
PBMA	poly(butyl methacrylate)
PMMA	poly(methyl methacrylate)
PS	polystyrene
PS-b-PEO-b-PS	polystyrene-block-poly(ethylene oxide) triblock copolymer
PS-b-PEO	polystyrene-block-poly(ethylene oxide) diblock copolymer
<i>Pt</i> BA	poly(<i>tert</i> -butyl acrylate)
RAFT	reversible addition fragmentation chain transfer
SEC	size exclusion chromatography
TEA	triethyl amine
wt %	weight percentage

SYMBOLS

AWR	wetting parameter of the paper surface in the z-direction
ΔC_p	specific heat (J/g. °C)
h	hour
$[I]_0$	initial concentration of the initiator (mol/L)
k_a	rate constant of activation
k_d	rate constant of dissociation
k_p	rate constant of propagation
L_m	ligand
$[M]_0$	initial monomer concentration (mol/L)
$[M]_t$	monomer concentration at any time (mol/L)
Met^n	transition metal at lower (n) oxidation state
Met^{n+1}	transition metal at higher (n+1) oxidation state
M_n	number average molecular weight (g/mol)
$M_{n,exp}$	experimental molecular weight (g/mol)
$M_{n,theo}$	theoretical molecular weight (g/mol)
$(Mwt)_0$	molecular weight of monomer (g/mol)
M_w	weight average molecular weight (g/mol)
M_w/M_n	polydispersity index
$\Delta[M]$	concentration of consumed monomer (mol/L)
$R\cdot$	carbon centred free radical
T_g	glass transition temperature (°C)
T_c	crystallization temperature (°C)
T_m	melt temperature (°C)
v %	per cent by volume
χ	Flory–Huggins interaction parameter

1 INTRODUCTION

1.1 Scope of the work

As a multicomponent system, atom transfer radical polymerization (ATRP) comprises a monomer, an initiator with a transferable atom (halogen in most cases), and a catalyst (composed of a transition metal species with any suitable ligand). Sometimes an additive (metal salt in higher oxidation state) is used. For successful ATRP, still other factors, such as solvent and temperature, must be taken into consideration.

This thesis describes the basic principles of ATRP and its application in the synthesis of homo- and block (co)polymers, and it reports tests of the prepared amphiphilic blockpolymers as coating agents for paper. Among the living radical polymerization systems ATRP was chosen because of its versatility and robustness. This is in contrast to nitroxide-mediated polymerization (NMP), which is limited to a certain type of monomer, and reversible addition fragmentation chain transfer polymerization (RAFT), which involves coloured and odoured thioesters.

The thesis summarizes the research reported in the five appended publications (I-V). First, ATRP of butyl methacrylate (*n*-BMA) both in bulk and in solution was undertaken to find the best conditions (initiator, solvent, and additive) for a more controlled synthesis of poly(*n*-butyl methacrylate) (I). A commercially available catalyst bistrisphenylphosphine iron(II) chloride tetrahydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}/\text{PPh}_3$), was employed. The synthesised polymer was used as macroinitiator for *tert*-butyl acrylate (*t*BA) in the preparation of the diblock copolymer poly(*n*-butyl methacrylate)-block-poly(*tert*-butyl acrylate) (PBMA-*b*-P*t*BA) (II). Some tetradentate nitrogen ligands were then synthesized, and used as complexing ligands in iron-mediated ATRP of methyl methacrylate (MMA) to study the effect of ligand bulkiness on the activity of the metal complex in ATRP (III).

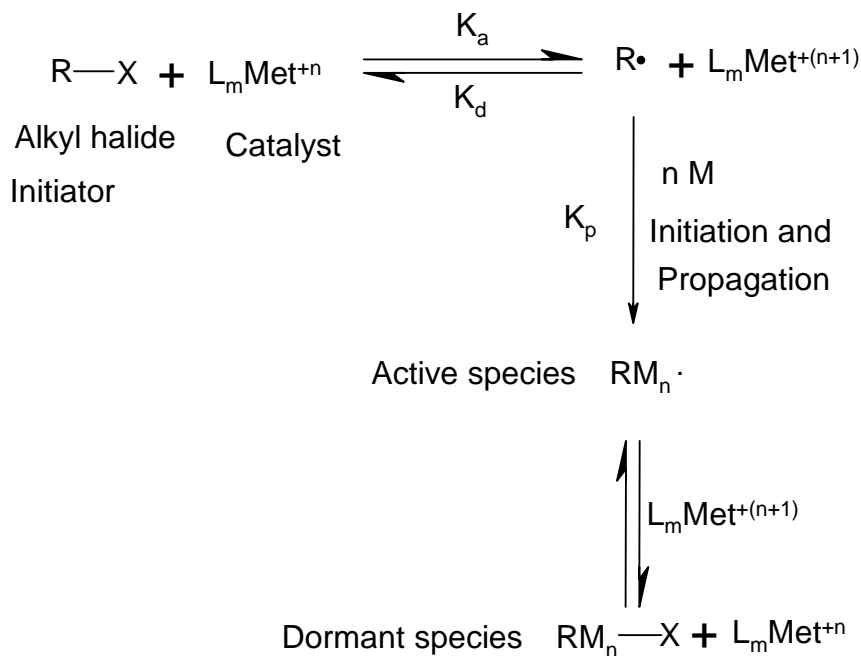
Finally, possibilities of applying block copolymers as coating materials on paper surface were investigated. A well-defined water-soluble/water-dispersible amphiphilic PMMA-*b*-PEO-*b*-PMMA triblock copolymer was prepared and characterized (IV), and its usefulness as coating on paper and model surfaces was investigated. Polystyrene-

poly(ethylene oxide) di- and triblock copolymers (PS-*b*-PEO, PS-*b*-PEO-*b*-PS) with well-defined molecular structure, unlike their counterparts, PMMA-*b*-PEO-*b*-PMMA were successfully applied as paper coating materials (V).

1.2 Atom transfer radical polymerization (ATRP)

Several methods of living/controlled radical polymerization have been developed in the past decade including nitroxide-mediated radical polymerization (NMP), reversible addition fragmentation chain transfer polymerization (RAFT) and atom transfer radical polymerization (ATRP).¹⁻⁴ Living polymerizations will lead to well-defined polymers only if the following prerequisites are met: initiation is fast in comparison with propagation, exchange between species of different activity is fast in comparison with propagation, and the rate of deactivation is low in comparison with propagation. ATRP is one of the most promising systems and has attracted wide research interests.⁵⁻¹⁶ It has proven to be efficient for a wide range of monomers (styrenes, meth(acrylates), acrylonitriles, etc.)⁹, polymerizing not only with Cu catalyst but with transition-metal complexes of Ru¹⁷, Pd¹⁸, Ni¹⁹, and Fe²⁰⁻²³. Polymerization is conducted either in bulk or in other solvents (benzene, water, etc.).^{24, 25} It is generally performed at moderate temperatures (70-130 °C). For all these reasons, ATRP has become a powerful tool for academic as well as industrial polymer chemists, allowing efficient synthesis of novel, tailor-made materials.^{9,10}

An extension of the atom transfer radical addition reaction, ATRP is based on the reversible deactivation of a propagating radical by transfer of (in most cases) a halogen atom from a transition metal complex in its higher oxidation state to the end of the growing polymer chain. The mechanism of ATRP is schematically depicted in Scheme 1, where R-X denotes an organic halide as initiating or dormant species and Met is the transition metal complex in lower (n) or higher (n+1) oxidation state.



Scheme 1. Schematic presentation of atom transfer radical polymerization (ATRP).

Initiation starts through halogen abstraction from the alkyl halide (with rate constant of activation k_a), resulting in a carbon-centred radical ($\text{R}\cdot$) and a metal whose oxidation state has increased by one (Met^{n+1}). After addition of one or more monomer units, the active radical reacts reversibly with the metal halide, with the rate constant of deactivation k_d , regenerating the lower oxidation state transition metal and a halogen end-capped oligomer. Polymer chains grow by the addition of free radicals to monomers in a manner similar to conventional radical polymerization, with the rate constant of propagation, k_p . However, by insuring that the reaction equilibrium favours the deactivated (dormant species) side, the number of radical species is kept low. At low concentration of radical species a minimum termination occurs.⁹ A successful ATRP will not only have a small contribution of terminated chains, but also a uniform growth of all chains, which is accomplished through fast initiation and rapid reversible deactivation.

The redox properties of the ATRP catalyst can be modified and its solubility increased by employing metal ligands such as 2,2 bipyridine and its derivatives or linear

amines.⁹ These ligands have been widely used in copper-mediated ATRP but rarely in iron-mediated ATRP.^{21, III}

Solvents influence the solubility of the catalyst, and the activity of the solution affects the kinetics of ATRP.²⁶⁻³² Matyjaszewski et al.²⁶ studied the ATRP of *n*-butyl acrylate (*n*-BA) in the presence of various solvents and found that polymerization appeared to be homogeneous when ethylene carbonate was used as a polar solvent, and it was faster in solution than in bulk. The solvent effect was also observed in the ATRP of methyl methacrylate (MMA) in the presence of toluene (50% v/v) and benzonitrile (25% and 50% v/v) where methyl 2-halo propionate was used as initiator and copper halide/bpy as catalyst.²⁷ The polymerization in more polar benzonitrile solution showed that number-average molecular weights were theoretically predictable ($M_n = (\Delta[M] / [I]_0) (Mwt)_0$, where M_n , $\Delta[M]$, $[I]_0$, and $(Mwt)_0$ present the average number molecular weight, concentration of consumed monomer, the initial concentration of the initiator, and the molecular weight of the monomer, respectively). Molecular weight distributions were narrow.²⁶⁻³¹ In addition to polar solvents, hydroxyl-containing solvents affect the rate of ATRP and accelerate the rate of polymerization.³²

Block copolymers containing acrylates are not only challenging synthetically but also interesting on account of their morphological and mechanical properties. Matyjaszewski and his co-workers have reported effective atom transfer radical polymerization of homo- and block (co)polymers of methacrylates,³³ methyl acrylates,³⁴ 2-hydroxy ethyl acrylates,³⁵ and tert-butyl acrylates.³⁶ However, there are very few reports on the synthesis of acrylates by iron-mediated ATRP.³⁷

1.3 Poly(ethylene oxide)-based amphiphilic block copolymers

Amphiphilic block copolymers are typical nonionic polymeric surfactants, which have attracted considerable attention for their outstanding solution properties and wide range of applications. These materials are highly interesting from the point of view of fundamental research, as they exhibit self-assembling properties in the presence of a selected solvent or surface.³⁸ Block copolymers consisting of dissimilar moieties, i.e. a hydrophilic moiety such as polyethylene oxide (PEO) and a hydrophobic moiety such as polystyrene (PS), poly(methyl methacrylate) (PMMA), or poly(butyl methacrylate)

(PBMA) are of interest for their potentially useful morphological properties (phase separation of the soft component from the hard one in addition to classical phase morphologies such as cylindrical and lamellar phase organization, etc.) and mechanical properties (elastic properties, deformation, elongation, etc.). When dissolved in a medium, that is a good solvent for one of the blocks and a nonsolvent for the other the amphiphilic block copolymers associate to form micelles. Each micelle consists of a core of the insoluble blocks surrounded by a solvent-swollen corona of the soluble block. In aqueous systems, block copolymers with polyethylene oxide as water-soluble part have attracted much attention in recent years and have been extensively reviewed.^{39-49, IV, V} Indeed, block copolymers tend to self-assemble into a wide variety of ordered structures (e.g. lamellar, hexagonal-packed cylinders).⁵⁰ To a certain extent, these structures can be controlled by varying the composition of the block copolymer and the segregation between blocks (via temperature or the degree of polymerization). The phase segregation between two domains is governed by the Flory–Huggins interaction parameter, χ , which is strongly influenced by the weight fraction of the various block copolymers.⁵¹ The ordered structures are realized through combination of a high glass transition temperature (T_g) block (hard block) with a low T_g block (soft block) and are highly attractive on account of their potential application as thermoplastic elastomers.^{52,53}

Diblock copolymers PS-b-PEO and triblock copolymers PS-b-PEO-b-PS have been particularly studied. Originally they were prepared by sequential anionic polymerization of styrene and ethylene oxide,⁵⁴ but more recently other systems, such as NMP⁵⁵ and ATRP, have been investigated. The first example of the synthesis of block copolymers PS-b-PEO-b-PS by ATRP was published by Kops et al. who reported the polymerization of styrene using 2000 g/mol 2-halo propionate telechelic poly(ethylene glycol) as macroinitiator⁵⁶. Similar studies were done by Ying et al.⁵⁷ for the synthesis of ABA block copolymers containing PS as A segment and different hydroxyl-terminated oligomers as B segment. The common feature of these studies was that the molecular weight of the macroinitiator did not exceed 5000 g/mol and polymerization was carried out in the presence of copper complexes. Matyjaszewski's group,⁵⁸ in turn, reported the synthesis of PMMA-b-PEO-b-PMMA triblock copolymers in a controlled manner via

ATRP as a first step toward the controlled synthesis of tissue engineering scaffolds. Their report focused on the physical and biological behaviour of these block copolymers.

Very recently, Wieser et al.⁵⁹ described the preparation of amphiphilic diblock copolymers made of poly(ethylene oxide) (PEO) and poly(hexyl methacrylate) (PHMA) synthesised by anionic polymerization of ethylene oxide and subsequent ATRP of HMA. The PEO block was prepared by anionic polymerization of ethylene oxide in tetrahydrofuran, end capping was achieved by treatment of living PEO chain ends with 2-bromoisobutyryl bromide to yield a macroinitiator for ATRP. The second block was added by polymerization of HMA, using the PEO macroinitiator in the presence of dibromobis(triphenylphosphine) nickel(II), $\text{NiBr}_2(\text{PPh}_3)_2$, as catalyst. Wieser et al.⁵⁹ suggested that PEO-block-PHMA block copolymers could be used as novel structure directing agents for the synthesis of nanostructured polymer-ceramic hybrid materials.

Before the present work, there were no reports in the literature on the synthesis of well-defined water-soluble/water-dispersible PEO-PMMA by ATRP in the presence of iron as the transition metal. Iron is an attractive transition metal in ATRP due to its low cost, availability, and nontoxicity. Moreover, no studies were found to indicate the feasibility of using PEO-PS amphiphilic block copolymers as coating materials in the paper industry. Malmström et al.⁶⁰ reported on the ATRP of methyl acrylate (MA) from initiators immobilized on cellulose fibres (preparation of PMA-grafted filter papers). The resulting polymer-grafted papers were extremely hydrophobic (contact angle 133°).

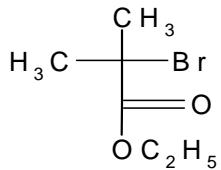
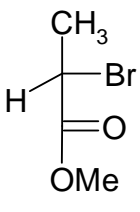
It is worth mentioning here that a major drawback of ATRP is the need for relatively large amounts of redox active transition metal, which makes product purification essential. The contamination of the polymer with the metal may be seen as a serious limitation for the industrial application of ATRP. To address this issue, a number of researchers have examined the use of immobilized catalysts,⁶¹⁻⁶⁵ where the catalyst is bound to an insoluble support such as silica or resin particles; however, these have tended to provide less control of the polymerization than unbound catalysts. Other ways to reduce the presence of catalyst in the final polymer product have been to utilize ion exchange resins,⁶⁶ a hybrid immobilized/soluble catalyst system,⁶⁷ ligands with temperature-variable solubilities,⁶⁸ or room temperature ionic liquids as solvents.⁶⁹⁻⁷²

2 Methods

2.1 Synthesis of homopolymers ^{I, II, III}

In a typical run of the polymerization, the monomer and the catalyst were introduced into a Schlenk glass tube, which was then capped by a two-way stopcock, purged with nitrogen in repeated vacuum/nitrogen cycles, and stirred by a magnetic stirrer. Solvent may or may not be used in this step. Initiator was then added under nitrogen with a syringe, and the glass reactor was immersed in an oil bath at the desired temperature for a specified reaction time. After the specified time, the reaction was stopped by withdrawing the tube and cooling the reaction mixture to room temperature. The mixture was diluted with tetrahydrofuran (THF). The obtained polymer solution was passed over alumina to remove the catalyst, after which the polymer was precipitated with an excess amount of methanol and dried under vacuum at room temperature until constant weight was obtained.

The table below summarizes the monomers and the corresponding initiators used in this study for homopolymerization.

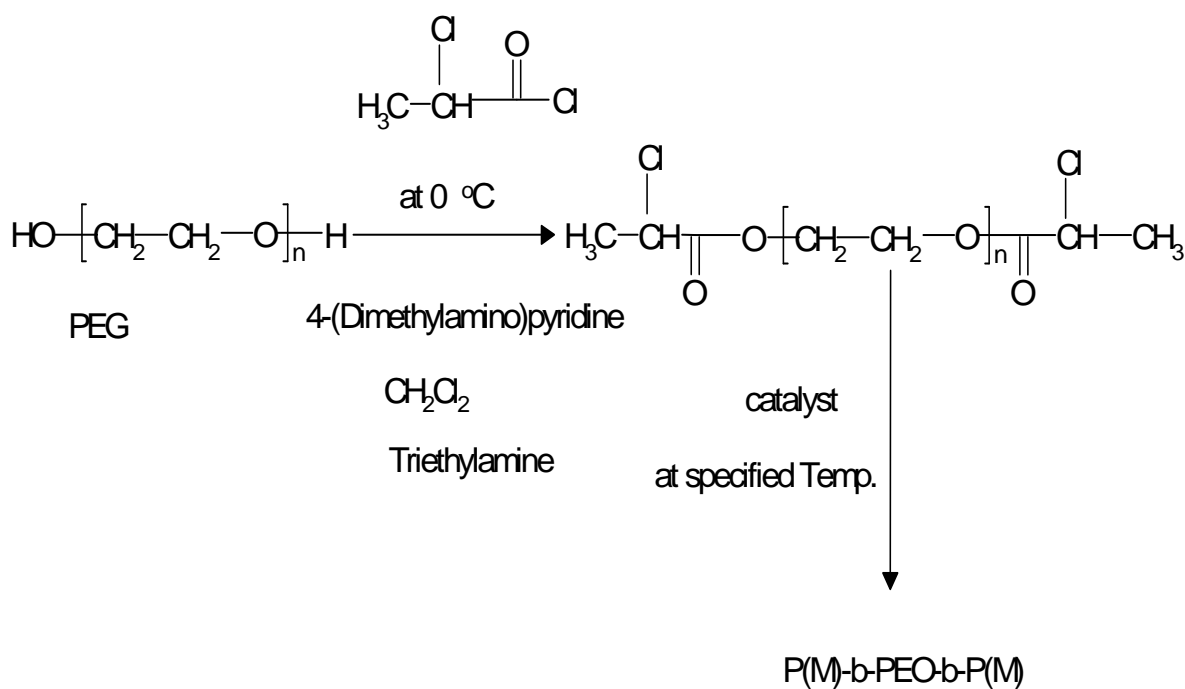
Monomer	Initiator
<i>n</i> -Butyl methacrylate (BMA), Methyl methacrylate (MMA)	 <p style="text-align: center;">2-Bromo ethyl isobutyrate</p>
<i>tert</i> -Butyl acrylate (<i>t</i> BA)	 <p style="text-align: center;">2-Bromo methyl propionate</p>

2.2 Synthesis of BMA-b-*t*BA block copolymers ^{II}

Block copolymers of (BMA-b-*t*BA) were prepared in the same way as homopolymers but at 110 °C with 25% (v/v) acetone as solvent, and with macroinitiator (PBMA) was added to the flask in powder form under nitrogen purge.

2.3 Synthesis of PEO-based amphiphilic block copolymers ^{IV, V}

Different amphiphilic block copolymers were synthesised in two steps according to the literature procedure⁵⁶ as outlined in Scheme 2.



Scheme 2. Preparation of PEO macroinitiator and the corresponding amphiphilic block copolymers.^{IV,V}

2.3.1 Preparation of PEO macroinitiators^{IV, V}

A 100-ml three-necked bottle was charged with triethylamine (TEA; 0.7 ml) and CH₂Cl₂ (10 ml) containing 4-(dimethylamino) pyridine (DMAP; 0.92 g) and was cooled to 0 °C under stirring. A solution of 2-bromopropionyl chloride (BPC; 1.3 ml) in CH₂Cl₂ (10 ml) was added. To the formed yellow dispersion of CH₂Cl₂, (50 ml) containing poly(ethylene glycol) (PEG) or monohydroxyl poly(ethylene glycol) (MPEG) (2.5 mmol) was added dropwise over 1 h. The reaction was kept at room temperature under N₂ for 18 h. The mixture was filtered to remove the formed ammonium salt and half of the solvent was removed by rotary evaporation, and the PEO macroinitiator was precipitated in cold diethyl ether. After dissolution in absolute ethanol, the solution was stored overnight to recrystallize the product. The product was then filtered, washed with ether, and dried in vacuum to give the PEO or MPEO macroinitiator as a white solid.

2.3.2 Preparation of PEO-based amphiphilic block copolymers^{IV, V}

The polymerization of the block copolymers was carried out under dry nitrogen in a dried Schlenk tube equipped with a magnetic stirring bar. The tube was charged with the required amounts of the macroinitiator and catalyst, sealed with a rubber septum, and degassed to remove oxygen. Degassed monomer (M) was added with a nitrogen-purged syringe, and the tube was degassed and backfilled with nitrogen three times. The contents were stirred for 5 min. Finally, the tube was immersed in an oil bath preheated to the desired temperature. After a given time, the reaction was stopped by withdrawing the tube and cooling the reaction mixture to room temperature. The crude products were dissolved in dichloromethane. The obtained polymer solution was passed over alumina to remove the catalyst, and the polymer was precipitated with an excess amount of hexane. The precipitated polymer was rinsed twice with distilled water at room temperature to remove possible unreacted PEO macroinitiator, immersed in cold diethyl ether, and dried in vacuum at room temperature.

2.4 Polymer characterization

The dried product was characterized by Fourier transform infrared spectroscopy (FT-IR), proton nuclear magnetic resonance (^1H NMR), and size exclusion chromatography (SEC) techniques, and the conversion was determined by gravimetry. FT-IR spectra of the macroinitiator and block copolymers were recorded on a Nicolet Magna FT-IR spectrometer using the KBr pellet technique. The ^1H NMR spectra of the polymer were recorded using a Varian Inc. (Palo Alto, CA) Gemini 2000XL NMR spectrometer operated at 300 MHz. The polymer solution was prepared by dissolving about 50 mg of polymer in 3 ml of deuterated chloroform (CDCl_3) or in deuterium oxide (D_2O).

The molecular weights were determined by room temperature SEC (Waters System Interface model, Waters 510 HPLC Pumps, Waters Differential Refractometer, Waters 700 satellite Wisp, and four linear PL gel column, 10^4 , 10^5 , 10^3 and 10^2 Å, connected in series). Chloroform was used as solvent and eluent. The samples were filtered through a 0.5 μm Millex SR filter. Injected volume was 200 μl and the flow rate was 1 ml min^{-1} . Nearly monodisperse polystyrene standards in the range 2×10^6 -150 g/mol were used for primary calibration.

Differential scanning calorimetry (DSC) runs were performed on a Perkin-Elmer DSC 7 apparatus equipped with a liquid nitrogen cooling system. Calibration was made with indium under a nitrogen atmosphere. Samples (18-20 mg) sealed in aluminium pans were quenched from room temperature to -60 $^\circ\text{C}$ and then scanned at 15 $^\circ\text{C/min}$ to +140 $^\circ\text{C}$, kept at this temperature for 5 min and then cooled back to -60 $^\circ\text{C}$ at 15 $^\circ\text{C/min}$. After 5 min at this temperature a final heating run was made at 15 $^\circ\text{C/min}$ to 140 $^\circ\text{C}$. Melting (T_m) and crystallization (T_c) temperatures were taken from the peak maxima in the second melting scan and the cooling scan, respectively. The values for the glass transition (T_g) are reported as the temperature by which one-half of the specific heat (ΔC_p) increase in glass transition region had occurred.

Dynamic mechanical analysis (DMA) technique (Perkin-Elmer DMA 7 in tensile mode) was used for some samples to confirm the presence or absence of phase

separation. Tensile films were prepared by solvent casting, and temperature sweeps were conducted from $-80\text{ }^{\circ}\text{C}$ at a heating rate of $4\text{ }^{\circ}\text{C}/\text{min}$.

Fine paper (FP) and light weight coated (LWC) paper were chosen for studies investigating the absorption characteristics of paper. FP was PM 7 from the Stora Enso Oulu Mill, which is producing offset paper grades. Chemical treatments were made on both the base paper and the final product (coated paper) while LWC paper was from UPM Kymmene Kaukas paper mill, which is producing printing grades. The same thing done for FP paper was also done for LWC paper.

For the ink penetration study, fine paper sheets were spray-coated with 1-3 weight% polymer solutions. Ink penetration was investigated with an Olympus BH2-HLSH optical microscope. The micrographs were taken from the coated side of the paper using tenfold magnification. A non-treated area was left on each sheets as a reference area. Lines were drawn on the coated and non-coated areas with a water-based felt pen to observe the penetration.

Polymers were also applied to a model silicon surface and characterized by optical microscopy and contact angle measurements. The optical images were recorded with a digital camera connected to a Leica MZ6 stereomicroscope. The static contact angles of water (distilled and deionized) were measured using a CAM 200 computer-controlled video-based instrument (KSV Instruments Ltd, Finland), and was analysed with software based on the Young-Laplace equation. The size of the water used in the test was $7\text{ }\mu\text{L}$.

3 RESULTS AND DISCUSSION

3.1 Synthesis of poly(butyl methacrylate) (*n*-BMA), poly(*tert*-butyl acrylate) (*t*BA) and the corresponding PBMA-*b*-PtBA copolymer

Two initiators were examined in testing the effect of initiator on ATRP polymerization of *n*-BMA in the presence of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}(\text{PPh}_3)_2$ as catalyst. The polymerization medium was homogeneous and darkly coloured, which indicated good solubility of the iron(II) complex. The kinetics of the bulk polymerization of BMA at 90 °C initiated by ethyl 2-bromo isobutyrate and α, α -dichloroacetophenone are presented in Figures 1 and 2.¹

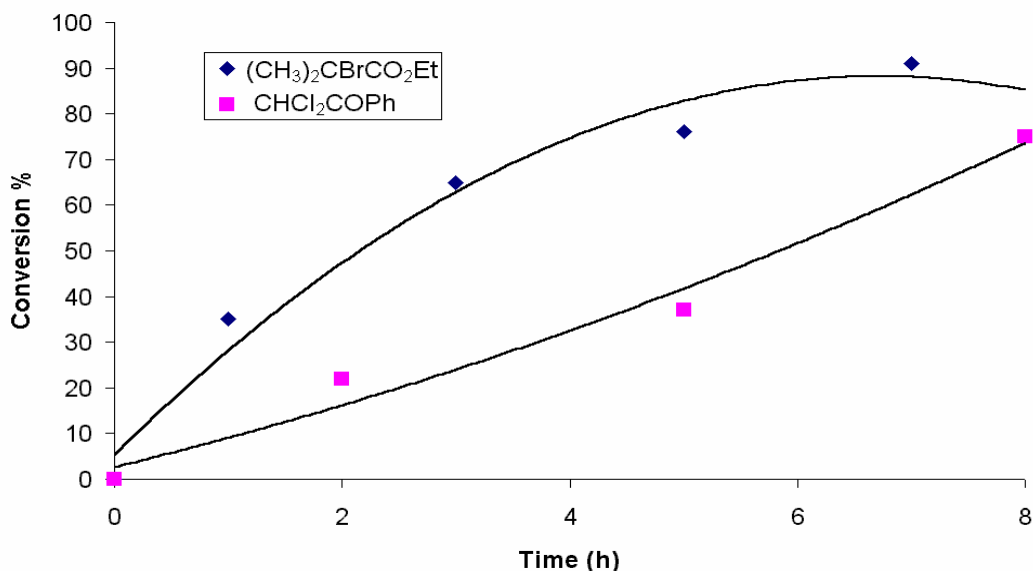


Figure 1. Bulk polymerization of BMA with $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}(\text{PPh}_3)_2$ as catalyst and $(\text{CH}_3)_2\text{CBrCO}_2\text{Et}$ or CHCl_2COPh as initiator at 90 °C ($[\text{Monomer}]/[\text{Initiator}]/[\text{Catalyst}] = 150/1/1$).¹

Figure 1 shows the increase of monomer conversion with time, which is a basic requirement for living systems. Figure 2, in turn, shows, the semi-logarithmic kinetic plot of $\ln ([\text{M}]_0/[\text{M}]_t)$ versus time, t , where $[\text{M}]_0$ is the initial concentration of the monomer, and $[\text{M}]_t$ is the monomer concentration at any time. The linearity of the plot indicates that

the concentration of growing radicals is constant. As can be seen from these figures, ethyl 2-bromoisobutyrate is a better initiator for BMA than is α,α -dichloroacetophenone. Evidently the structure of the alkyl group in ethyl 2-bromoisobutyrate is similar to the structure of the dormant polymer species, and this induces better homogeneity to the system.^{9, I}

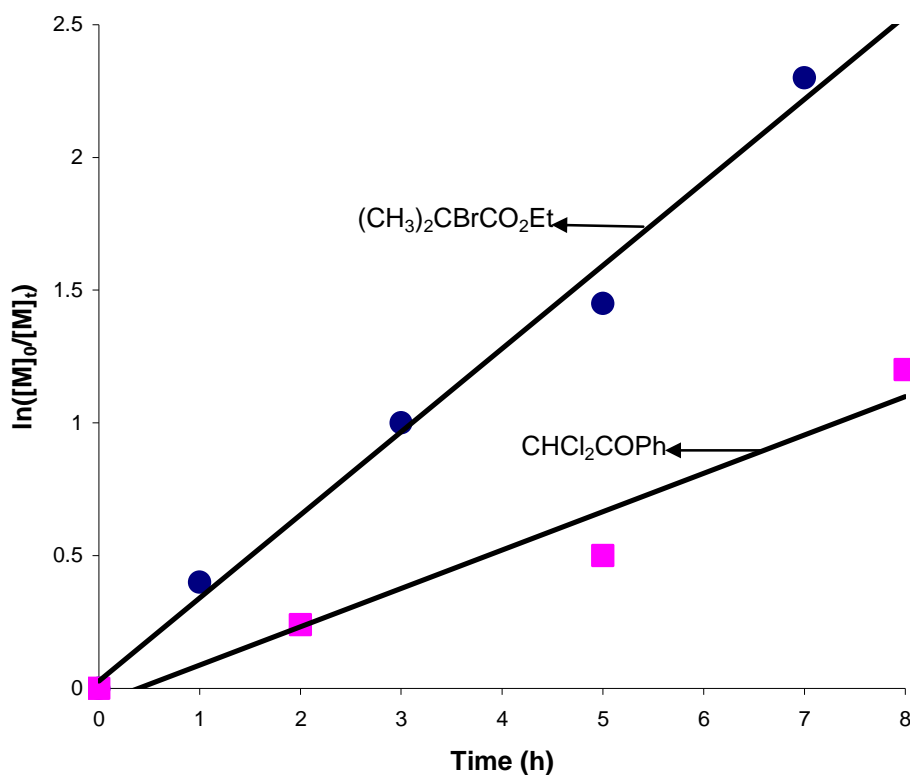


Figure 2. First order kinetic plot of $\ln([M]_0/[M]_t)$ versus time in the bulk polymerization of BMA at 90 °C with $(CH_3)_2CBrCO_2Et$ or $CHCl_2COPh$ as initiator ($[Monomer]/[Initiator]/[Catalyst] = 150/1/1$).^I

Polymerization of tert-butyl acrylate (*t*BA) has been conducted using various techniques, including ionic,⁷³ nitroxide-mediated,^{74, 75} and metallocene catalyst-mediated reactions.⁷⁶ A variety of acrylate monomers have been polymerized efficiently by ATRP technique,^{77-87, II} but, most of them with Cu/bipyridine catalyst systems.

Unlike the butyl methacrylate system, polymerization of *t*BA in the presence of $FeCl_2 \cdot 4H_2O(PPh_3)_2$ catalyst in bulk was heterogeneous. Because of this heterogeneity, a search was made for the optimal conditions for the polymerization.^{II} Table 1 summarizes

the tested conditions and the characteristics of the poly(*tert*-butyl acrylate) obtained by ATRP.

Table 1. ATRP of *t*BA using $FeCl_2 \cdot 4H_2O(PPh_3)_2$ catalyst system and initiated by methyl 2-bromopropionate, under various conditions, in bulk. **II**

Entry	[Monomer]/ [Initiator]	Temperature (°C)	Time (h)	Conversion (%)	$M_{n,exp}$ (g/mol)	$M_{n,theo}^a$ (g/mol)	M_w/M_n
1	200/1	110	1	90	22800	23000	1.98
2	200/1	90	2	60	13000	15400	2.17
3	150/1	70	2	80	18900	15400	2.14
4	150/1	110	0.5	30	10000	5800	1.80
			1	72	16300	13900	2.00
			2	90	17000	17300	1.90

^a $M_{n,theo} = 128([tBA]_0 / [\text{methyl 2-bromo propionate}]_0 \times \text{conversion})$

Entry 1 in Table 1 appears to give very fast reaction (90% conversion in 1 h) and the theoretical number average molecular weight, $M_{n,theo}$, is in good agreement with the experimental value, $M_{n,exp}$, obtained by gel permeation chromatography (GPC); but the polydispersity (M_w/M_n) is rather high. More detailed information concerning the optimizing of conditions can be found in publication **II**.

Matyjaszewski's group³⁷ used CuBr/PMDETH (pentamethyldiethylenetriamine) as catalyst system in the bulk polymerization of *t*BA to obtain the target system with high molecular weights (monomer-to-initiator ratio of 400). They synthesised *t*BA polymers with polydispersities as low as 1.22, but there was a significant deviation between their experimental and theoretical molecular weights, particularly at higher conversions. This was attributed to the differences in hydrodynamic volumes between the poly(*t*BA) and linear polystyrene standards.

Introducing a slightly polar solvent (acetone) proved to be an efficient way to synthesise polymers with controlled properties, since the solubility of the catalyst was improved.³⁷

Figures 3 and 4 show the ATRP kinetics of the solution polymerization of *t*BA, which was carried out with methyl 2-bromopropionate as initiator.

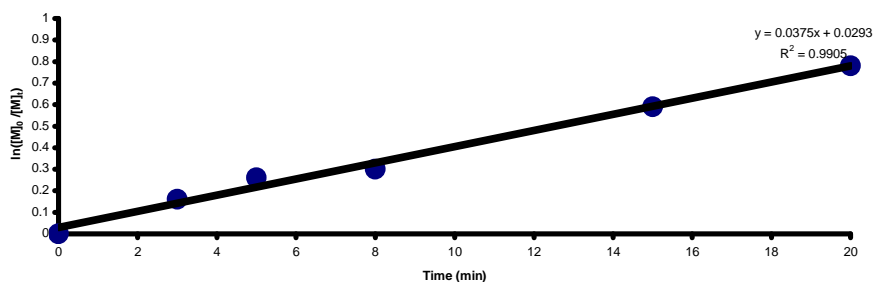


Figure 3. First order kinetic plot of $\ln([M]_0/[M]_t)$ versus time in solution polymerization of *t*BA with $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}(\text{PPh}_3)_2$ as catalyst and $\text{CH}_3\text{CHBrCO}_2\text{CH}_3$ as initiator at 110°C ($[\text{Monomer}]/[\text{Initiator}]/[\text{Catalyst}] = 200/1/1$).^{II}

Figure 3 shows the semi-logarithmic plot of the heterogeneous ATRP of *t*BA in 33%(v/v) acetone. The plot of $\ln ([M]_0/[M]_t)$ versus time is linear and of first order indicating a constant number of propagating species throughout the reaction.

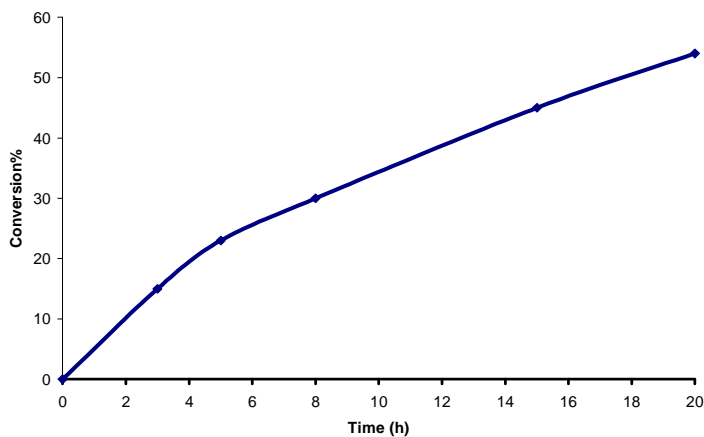


Figure 4. Solution polymerization of *t*BA with $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}(\text{PPh}_3)_2$ as catalyst and $\text{CH}_3\text{CHBrCO}_2\text{CH}_3$ as initiator in (33% v/v) acetone at 110°C ($[\text{Monomer}]/[\text{Initiator}]/[\text{Catalyst}] = 200/1/1$).^{II}

Figure 4 shows the dependence of conversion on time for the *t*BA monomer. As can be seen, the consumption rate of *t*BA evolves with time and the reaction rate of *t*BA during the polymerization process is slow (54% conversion in 20 h).

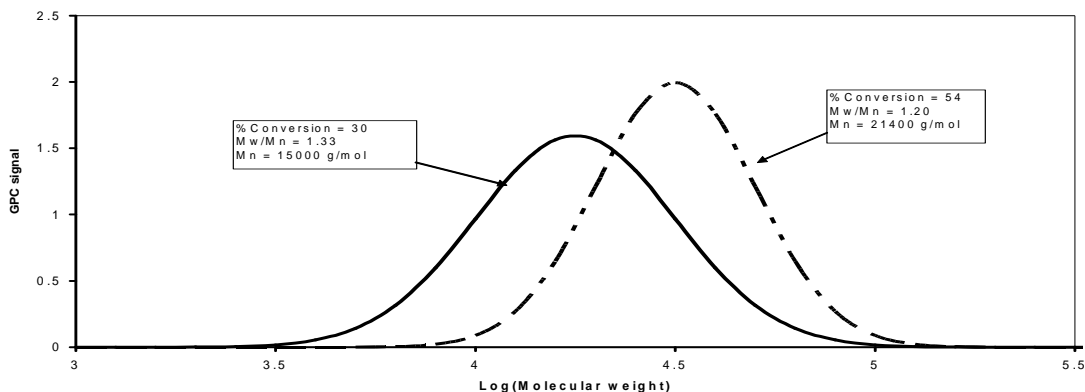


Figure 5. GPC curves of *Pt*BA obtained under the same conditions as in Figure 3.^{II}

The GPC curves of poly(*tert*-butyl acrylate), *Pt*BA, which are single and symmetric peaks, are depicted in Figure 5. The large increase in the molecular weights and the low polydispersities with unimodal shapes of the GPC traces of the chain-extended polymers demonstrate the success of the chain-extension.

Block copolymerization of BMA-*b-t*BA was conducted using a two-step ATRP method. The first step was the synthesis of macroinitiator (PBMA)^I (see above in this section). The second step was to add a low conversion PBMA macroinitiator (conversion =35%). Low conversion macroinitiator was used to avoid loss of halogen during ATRP synthesis of PBMA-*b-Pt*BA block copolymers. Figure 6 presents the GPC chromatograms of PBMA and PBMA-*b-Pt*BA obtained under the following reaction conditions: [*t*BA]/[PBMA]/[FeCl₂.4H₂O(PPh₃)₂] 1000/1/1 at 110 °C in 25% (v/v) acetone (reaction time 15 h). As a result of the chain-extension reaction, the molecular weight was increased from $M_n = 7650$ g/mol, $M_w/M_n = 1.38$, to $M_n = 15400$ g/mol, $M_w/M_n = 1.55$. The obtained block copolymer showed no tail on the low molecular weight, i.e. no remaining PBMA macroinitiator.

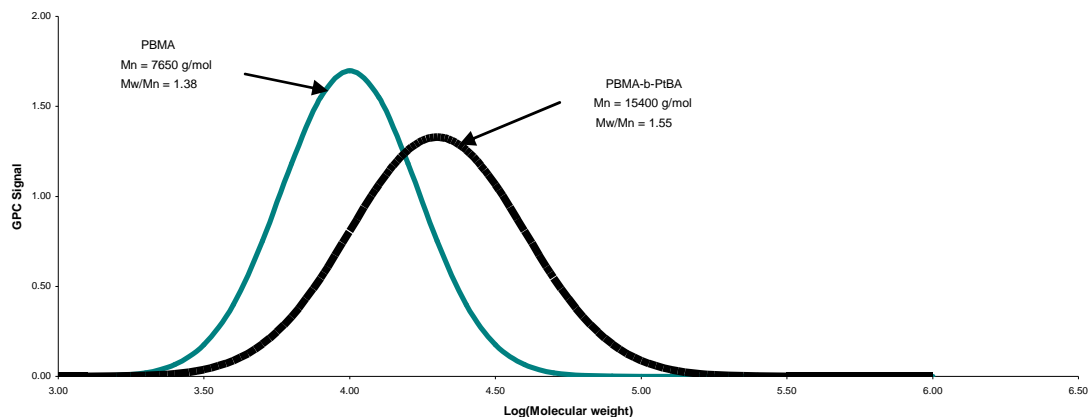


Figure 6. GPC chromatograms of PBMA macroinitiator and PBMA-*b*-PtBA diblock copolymer.^{II}

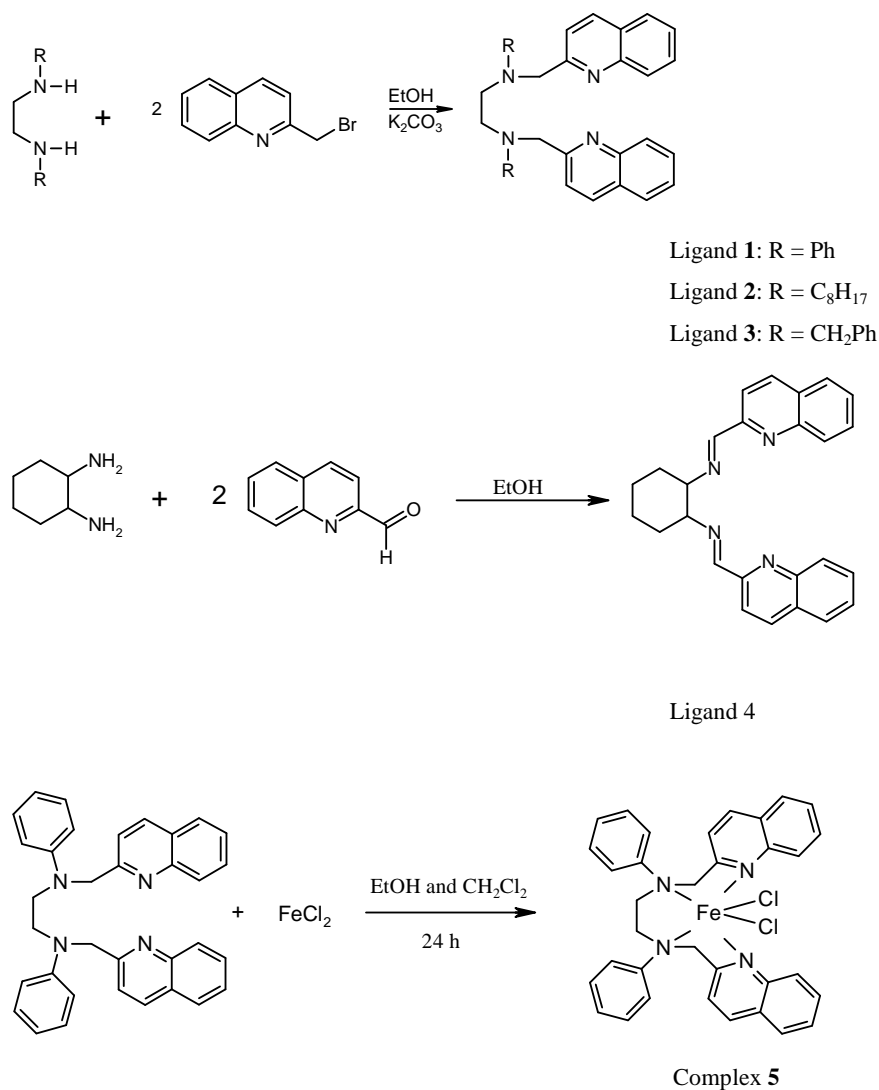
Figure 6 shows how the GPC chromatogram of macroinitiator PBMA is shifted to a higher molecular weight position, upon the formation of diblock copolymer, PBMA-*b*-PtBA.

3.2 Polymerization of methyl methacrylate in the presence of iron(II) complex with tetradentate nitrogen ligands^{III}

Multidentate nitrogen ligands work well in copper-mediated ATRP, providing the desired reactivity.⁹ Recently, iron-based catalysts containing imine ligands have drawn a great deal of attention in ATRP.^{88, 89} Gibson and co-workers used FeCl₂ complexes bearing α -diimine ligands for the ATRP polymerization of MMA⁸⁸ and styrene.⁸⁹ The α -diimine ligands containing alkylimino substituents induced well-controlled ATRP of both MMA and styrene, whereas ligands with arylimino substituents gave rise to chain-transfer processes.

In the experiments of this section polymerization, of MMA was performed using iron as the transition metal with different tetradentate nitrogen coordinated ligands in an attempt to understand the influence of these ligands on polymer properties. Ligands **1-4** (dichloro{[N,N'-diphenyl-N,N'-di(quinoline-2-methyl)]-1,2-ethylene diamine} (**1**),

{[N,N'-dioctyl-N,N'-di(quinoline-2-methyl)]-1,2-ethylene diamine} (**2**), {[N,N'-dibenzyl-N,N'-di(quinoline-2-methyl)]-1,2-ethylene diamine} (**3**), and (1R,2R)-(-)-N,N'-di(quinoline-2-methyl) di-iminocyclohexane (**4**) were synthesised as shown in Scheme 3.⁹⁰ All these ligands were synthesised at the Laboratory of Inorganic Chemistry, University of Helsinki. Ligands **1** and **2** were synthesised for the first time, while ligands **3** and **4**, which were synthesised earlier, were used here as ATRP ligands for the first time.



Scheme 3. Synthesis routes for the tetradentate ligands **1-4** and complex **5**.^{III}

It was essential as noted above, to optimize the amount of catalyst in ATRP polymerization of MMA since, the metal is considered as a contaminant of the polymer. Accordingly, the effect of molar ratio of catalyst to initiator was studied carefully. Table 2 shows that the polymerization results were very good when the molar ratio was 1. When the ratio was decreased from 1.0 to 0.25, slower polymerization and broader molecular weight distribution was obtained, possibly due to more frequent termination reactions during the early stage of the polymerization.

Table 2. Characteristics of the MMA polymerization with ligand 1. ^{a, III}

Entry	Catalyst	[Cat]/[In]	%Conversion	Polydispersity	M _{n,exp} (g/mol)	M _{n,theo} (g/mol)
1	1 + FeCl₂	1	87.5	1.35	26000	26250
2	1 + FeCl₂	0.5	48	1.55	20700	14400
3	1 + FeCl₂	0.25	29	1.58	21000	8700

^aconditions: T = 90 °C, [monomer]/[initiator] = 200/1, [catalyst]/[ligand] = 1/1, time = 90 min, solvent, o-xylene, 33% v/v)

It is of interest to mention here that when iron(II) chloride was replaced with copper(I) chloride (Cu is superior as ATRP transition metal), the result was poor control of polydispersities and molecular weights. Similar results have been reported by Zhu and Yan.⁹¹

The same conditions as used with ligand **1** were used for the polymerization of MMA with ligand **2**. Table 3, entry 1, shows good ATRP results after a reaction time of 10 minutes ($M_w/M_n = 1.27$), but after 40 minutes (entry 4) the polymer was rigid and control was lost. Similar behaviour was found by Göbelt and Matyjazewski⁹² in polymerization of MMA initiated by 2-bromopropionitrile and catalysed by diiminopyridine/FeBr₂ complex. Their reaction was not controlled ($M_w/M_n=1.21$ for 5% conversion and 1.68 for 42% conversion; M_n (GPC) was higher than M_n ,theo). On the basis of ours and their results, we conclude that a ligand with long aliphatic chain on the nitrogen atoms provides solubility of its metal complexes in organic solvents. However, increasing length of the alkyl substituents also induces steric effects, which play an

important role in determining the position of the equilibrium between dormant and active polymer chains.

Table 3. Results of the ATRP polymerization of MMA using ligand 2^{a, III}

Entry	Time (min)	Conversion, %	M_w/M_n	$M_{n,exp}$ (g/mol)	$M_{n,theo}$ (g/mol)
1	10	16	1.27	15000	3200
2	20	27	1.36	23000	5400
3	30	43	1.55	27000	8600
4	40	53	2.40	61500	10600

^aconditions: T= 90 °C, solvent, o-xylene(33%(v/v)[monomer]/[initiator]/[catalyst]/[ligand] = 200/1/1/1.

Table 4 summarizes the results of the polymerization experiments when ligand **3** which is bulkier than ligands **1** and **2** was introduced. As the bulkiness around the nitrogen increases, ATRP becomes uncontrolled and the polymers exhibit higher molecular weights, broader molecular weight distributions, and lower rates of reaction in relation to ligands **1** and **2**. Ligand **4** was not at all efficient for ATRP polymerization of MMA under the same conditions as for the other ligands.^{III} (No polymer was formed after 4 h and only traces after 7 h).

Table 4. Results of the ATRP polymerization of MMA using ligand 3^{a, III}

Entry	Ligand	Time (h)	Conversion, %	M_w/M_n	$M_{n,exp}$ (g/mol)
1	3	1	8	1.8	550000
2	3	2	21	2.0	555000
3	3	3	53	1.8	500000

^aconditions: T = 90 °C, solvent, o-xylene(33%(v/v),[monomer]/[initiator]/[catalyst]/[ligand] = 200/1/1/1

It is worth mentioning that these ligands were used in *tert*-butylacrylate (*t*BA) polymerization after activation with methylaluminumoxane (MAO). In general, polyacrylates with high molecular weights and narrow polydispersities ($M_w/M_n \sim 2$) were obtained.⁹⁰

3.3 Synthesis of amphiphilic PEO-*b*-PMMA/PS water-soluble/water-dispersible block copolymers^{IV, V}

Water-soluble amphiphilic polymers are of particular interest due to the presence of microdomains which may impart unusual reactivity to a chemical system. Moreover, amphiphilic polymers are of low toxicity when water is used as solvent.

Esterification of a hydroxyl group of a macromolecule with halogenated acyl halide (Scheme 2) proved to be an excellent method for producing macroinitiators suitable for ATRP.^{56, 93, 94} With this approach, a number of amphiphilic block copolymers were synthesised from poly(ethylene oxide) PEO macroinitiators.⁹⁵⁻¹⁰³

Boschet et al.¹⁰⁴ report that when the initial weight percentage of the hydrophobic comonomer exceeds 10 wt-%, the corresponding copolymer is not soluble in water. A series of PMMA-*b*-PEO-*b*-PMMA triblock copolymers and PS-*b*-PEO di- and triblock copolymers with different molecular weights and compositions were synthesised by ATRP technique. In the case of the PMMA copolymers the molecular weights of PEO were 20,000 g/mol for A1, A2, A3, and A4; 10,000 g/mol for B; 6000 g/mol for C1, C2, and C3; and 2000 g/mol for D1 and D2 (Table 5).

Table 5. Characteristics of water-soluble PMMA-*b*-PEO-*b*-PMMA triblock Copolymers synthesised with the FeCl₂.4H₂O/PPh₃ catalytic system.^{IV}

Sample	wt-%MMA	M _n (theo) (g/mol)	M _n (GPC) (g/mol)	M _w /M _n	Solubility in water
A1	5	21200	34700	1.21	soluble
A2	8	22000	32200	1.13	soluble
A3	15	23500	28000	1.25	dispersible
A4	20	25100	31000	1.27	dispersible
B	9	11000	15500	1.31	soluble
C1	5	6300	13200	1.02	soluble
C2	8	6500	12000	1.15	soluble
C3	15	7100	13000	1.03	dispersible
D1	5	2100	4800	1.09	soluble
D2	8	2200	5000	1.16	soluble

The results of the molecular characterization of the water-soluble/water-dispersible PMMA-*b*-PEO-*b*-PMMA triblock copolymers presented in table 5 show that controlled water-soluble copolymers were synthesised by means of the FeCl₂.4H₂O/PPh₃ catalytic system.

In the same manner as for PMMA-*b*-PEO-*b*-PMMA triblock copolymers, a series of PS-*b*-PEO di- and triblock copolymers with different molecular weights and compositions were synthesised with the (CuCl/bipy) catalytic system. Molecular weight of PEO for samples 1 and 2 was 2,000 g/mol, for samples 3 and 4 was 6,000 g/mol, for samples 5, 6, and 7 was 10,000 g/mol, and for samples 8 and 9 it was 20,000 g/mol.

Table 6 shows the results of molecular characterization of water-soluble/water-dispersible di- and triblock copolymers of PS-*b*-PEO.

Table 6. Characteristics of water-soluble/water-dispersible PS-*b*-PEO di and triblock copolymers.^v

Sample	wt-% PS/FPS	Block copolymer	M _n (theo) (g/mol)	M _n (GPC) (g/mol)	M _w /M _n	Solubility in water
1	5	PS-PEO(2K)-PS	2100	5000	1.28	soluble
2	7	PS-PEO(2K)-PS	2200	4700	1.22	soluble
3	7	PS-PEO(6K)-PS	7200	7050	1.29	soluble
4	9	PS-PEO(6K)-PS	7600	7500	1.26	soluble
5	5	PS-PEO(10K)-PS	10650	18000	1.07	soluble
6	7	PS-PEO(10K)-PS	10750	18000	1.09	soluble
7	10	PS-PEO(10K)-PS	11000	19000	1.07	milky dispersion
8	9	PS-PEO(10K)-PS	11000	18000	1.17	soluble/turbid
9	5	PS-PEO(20K)-PS	23500	18400	1.4	soluble
10	7	PS-PEO(20K)-PS	25300	20500	1.35	soluble
11	9	PS-PEO(5K)	6000	6500	1.19	soluble
12	10	PFS-PEO(5K)	5600	9600	1.13	dispersible
13	10	PFS-PEO(10K)-PFS	11100	20000	1.09	dispersible

Tables 5 and 6 confirm that amphiphilic block copolymers with low polydispersities (which is the character of controlled/living polymerization) could be successfully synthesised by ATRP method using either iron (for PMMA) or copper (for PS) as the transition metal. Well-defined di- and triblock copolymers were synthesised using PEO as macroinitiator.

3.3.1 Thermal characteristics of PMMA-*b*-PEO-*b*-PMMA triblock copolymers^{IV}

Since PEO is a semicrystalline polymer, its properties are related to its morphological features such as degree of crystallization and size and perfection of crystallites. It is important, therefore, to study the crystallization behaviour of amphiphilic block copolymer containing PEO as hydrophilic and crystallizable segment.

Table 7. “Thermal characteristics” of PEG- homopolymers, corresponding macroinitiators, and water-soluble/water-dispersible PMMA-*b*-PEO-*b*-PMMA triblock copolymers. ^{IV}

Polymer		T _m (°C)	T _c (°C)	T _g PEG (°C)	T _g PMMA (°C)
PMMA					122
PEG 20K	(A)	68	37	-39	
PEG 10K	(B)	68	38	-42	
PEG 6K	(C)	65	40	-39	
PEG 2K	(D)	61	26	-40	
macroinitiator					
Cl-PEO 20K-Cl		64	35	-39	
Cl-PEO 10K-Cl		61	32	-39	
Cl-PEO 6K-Cl		55	28	-39	
Cl-PEO 2K-Cl		43	21	-37	
block copolymer wt-%MMA					
A1	5	62	30	-39	100
A2	8	63	26	-39	100
A3	15	58	24	-39	100
A4	20	59	25	n.d.	100
B	9	56	1+(32)	-39	100
C1	5	56	27	-39	100
C2	8	54	26	-39	100
C3	15	51	21	-39	99
D1	5	43	15	-39	99
D2	8	44	17	-39	99

To understand the relationship between the PMMA block and crystallization of PEO, the crystallization behaviour of PMMA-*b*-PEO-*b*-PMMA copolymers was investigated by DSC, and the obtained data are summarized in Table 7. Melting and crystallization temperatures are lower for the poly(ethylene oxide) blocks in all triblock copolymers than for the pure PEGs precursors. Interestingly, copolymer B crystallized very slowly, perhaps due to a fractionated crystallization process, leading to PEO confined into cylinders or spheres.¹⁰⁵

The melting endotherms of the two block copolymers A1 and A4 and the corresponding macroinitiator Cl-PEO(20K)-Cl used in their synthesis are displayed in Figure 7. The melting point of PEO decreases with increasing block length of PMMA.

The inset curves in Figure 7 show the presence of two glass transitions, suggesting that the block copolymers are phase separated. In general, in using T_g in determination of

polymer miscibility, it is assumed that the observation of a single T_g between those of the pure components indicates miscibility, whereas the appearance of two T_g s stands for occurrence of phase separation.

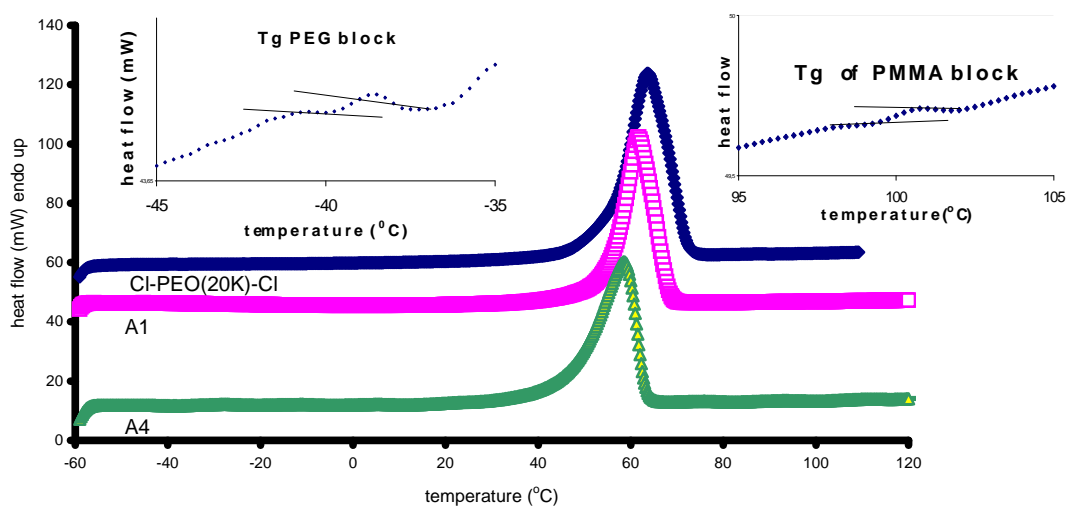


Figure 7. Melting curves of the water-soluble/dispersible triblock copolymers A1 and A4 and the corresponding macroinitiator Cl-PEO(20K)-Cl. The inserts show the T_g transitions of the PEO and PMMA blocks.^{IV}

3.3.2 ^1H NMR behaviour of PS-*b*-PEO-*b*-PS triblock copolymer in aqueous solution

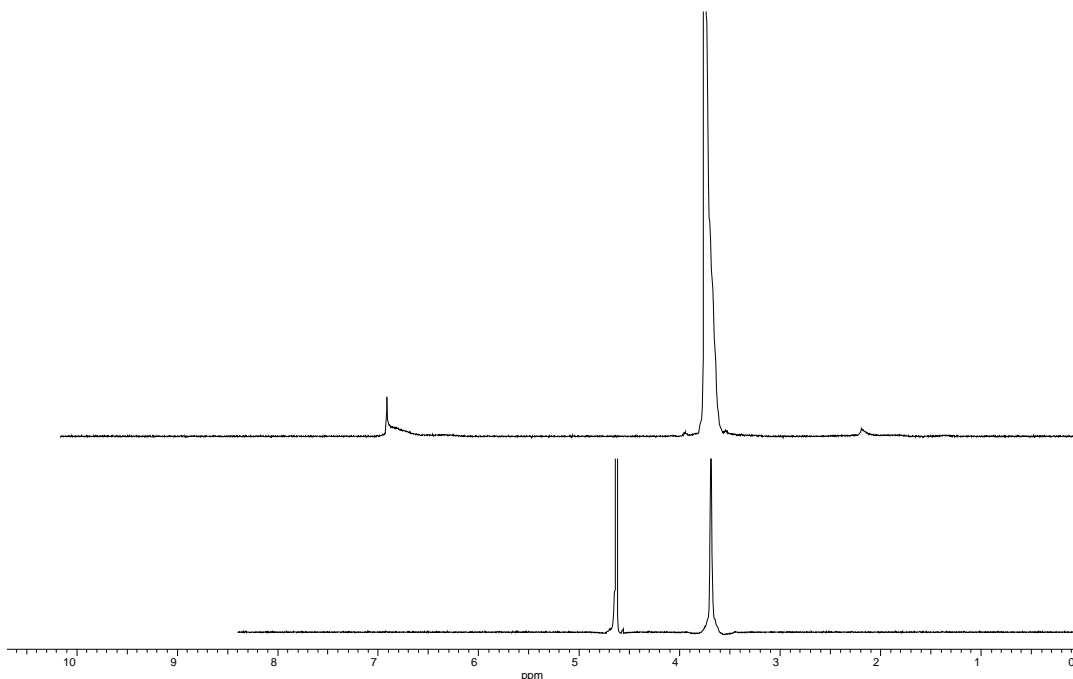


Figure 8. ^1H -NMR spectra of PS-*b*-PEO-*b*-PS triblock copolymer (sample 6 Table 6 in CDCl_3 (top) and D_2O (below) solvents).

Figure 8 shows the ^1H -NMR spectra of PS-*b*-PEO-*b*-PS in CDCl_3 and D_2O solvents. When CDCl_3 solvent was used, $\delta = 3.64$ appeared for methylene protons of PEO blocks, and $\delta = 6.5$ and 7.2 for the phenyl ring protons of PS blocks. In D_2O solvent, however, $\delta = 3.64$ again appeared for the methylene protons of PEO blocks, but the peaks ascribed to the phenyl ring protons of PS blocks were not seen. The disappearance of the peaks for phenyl ring protons indicated that aggregates had been formed. CDCl_3 is a good solvent for both PS and PEO blocks, and the block copolymer chains were mostly extended in the solution. Although D_2O is a good solvent for PEO blocks, it is a poor solvent for PS blocks, and, as a consequence, the chains of the triblock copolymers tended to self-assemble and associated, forming aggregates with inner insoluble PS blocks and outer soluble PEO blocks.

3.4 Application of PEO-PS amphiphilic block copolymers as paper coating

materials

Water-soluble/water-dispersible block copolymers (Table 6), were coated on paper and model surfaces to study their effects on the absorption and spreading ink.

3.4.1 Polymers on silicon model surfaces: study of orientation and hydrophobicity^V

Spin coating was used to obtain a rough idea of the the morphology of the polymer layer di- and triblock copolymers on silicon model surfaces. The copolymer (samples 11 and 8) (Table 6) were applied on silicon surfaces as 3 w-% aqueous solutions. Optical microscopy was used, as well as contact angle measurements, to explore the hydrophobicity of the surface, and gain an idea of the orientation of the polymers. Figure 8 presents the optical microscopic images of sample 11 (diblock copolymer) and sample 8 (triblock copolymer) on the hydrophilic silicon surface. Sample 11 (Figure 8 (a)) forms a continuous layer, whereas sample 8 (Figure 8 (b)) forms a more heterogeneous layer consisting of a macroscopic precipitate and a thin adsorbed polymer layer with lamellar crystal patterns. There is also a difference in the aqueous solutions: the solution of sample 11 is clear, whereas that of sample 8 is turbid. These differences originate from the block structures of the polymers. Moreover, the diblock structure allows the formation of more ordered micelle-like particles solubilized by hydrophilic PEO blocks. The hydrophobic PS end groups on the triblock copolymer, however, induce bridging between the micellar subunits leading to formation of larger and less ordered aggregates. Accordingly, during the drying phase in spin coating, the increasing concentration leads to formation of a macroscopic precipitate in the case of the triblock copolymer (sample 8), whereas in the case of the diblock copolymer (sample 11) the particles are more sterically stabilized and a continuous layer is formed.

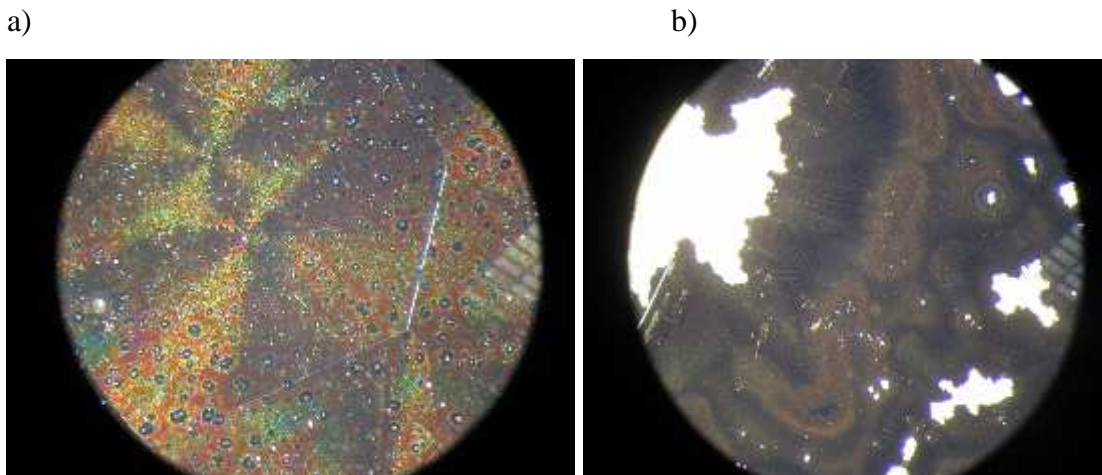


Figure 8. Optical microscope images of a) sample 11 (diblock copolymer) and b) sample 8 (triblock copolymer) on silicon surface.

3.4.2 Behaviour of polymers on paper surfaces ^{V,*}

Figures 9 and 10 show that base papers become more hydrophilic when treated with pure PEO polymers (2k, 10k, and 20k). The change can be followed by the contact angle of water (Figure 9), which is lower, and by the polarity component, which is higher, for the treated papers than for the untreated reference papers. In the case of the PS-*b*-PEO-*b*-PS sample in which weight per cent of PS is 5 wt-% (sample 5, Table 6), there is no change in hydrophobicity/hydrophilicity relative to the pure PEO polymer. The situation is different when the amount of PS is 7 wt-% (sample 6). Both wood-free and wood-containing are less hydrophilic when coated with this polymer than when coated with pure PEO (10k) or PEO (20k) or with PS-*b*-PEO-*b*-PS containing 5 wt-% PS (sample 5). In fact, coating with PS-*b*-PEO-*b*-PS with 7 wt-% PS (sample 6) has virtually no effect on the hydrophobicity or hydrophilicity of wood containing paper compared to untreated reference paper (Figure 10).

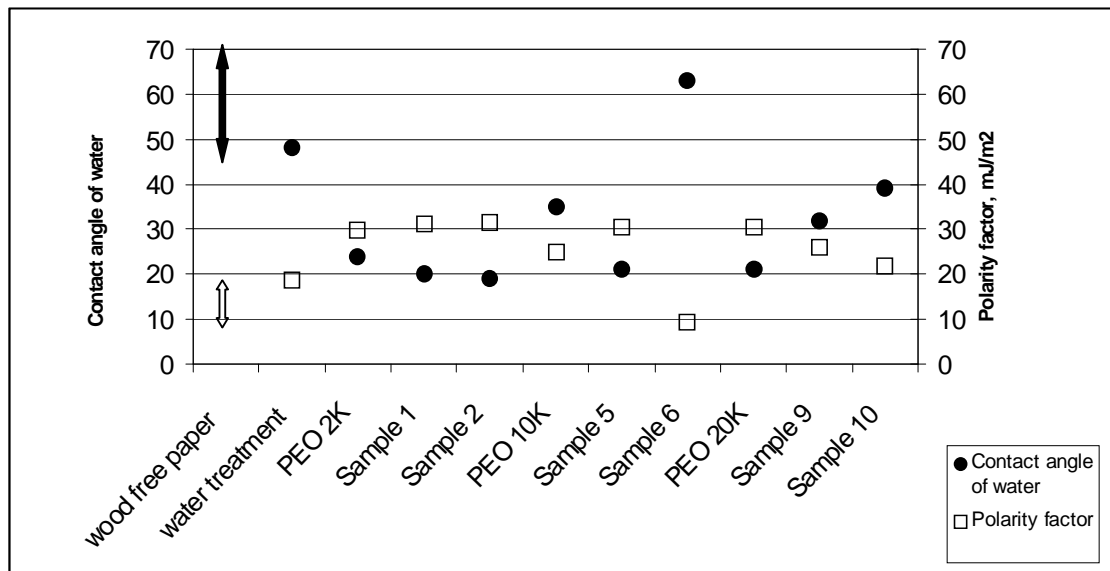


Figure 9. The contact angle of water and the polarity factor of surface energy on polymer-coated FP base paper^v (samples from Table 6).

* Contact angle measurements were done by Kirsi Kataja at VTT.

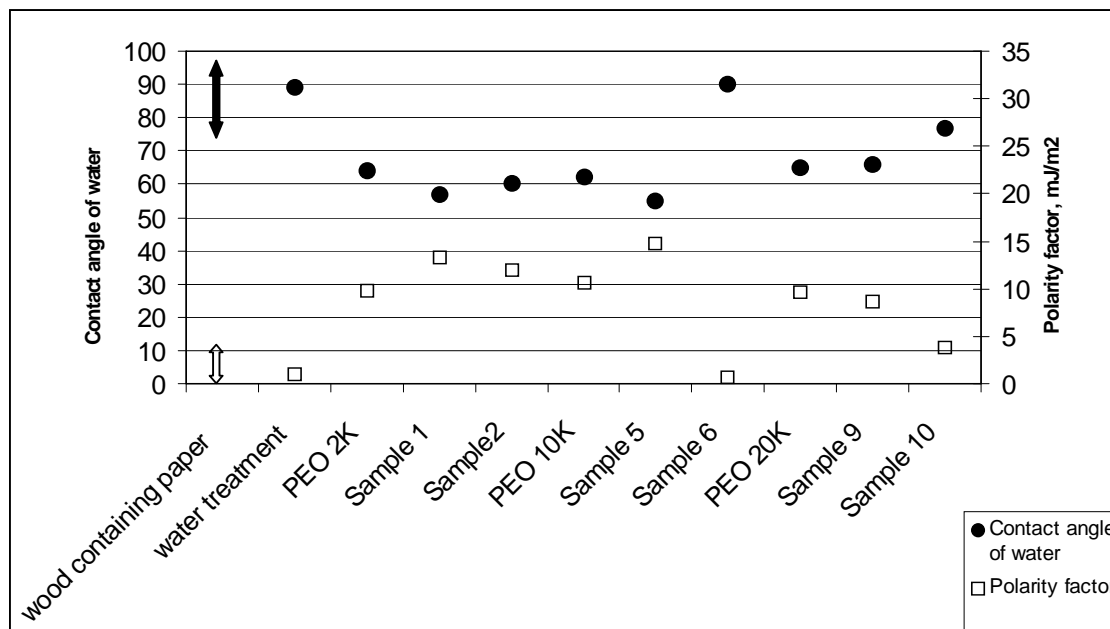


Figure 10. The contact angle of water and the polarity factor of surface energy on polymer-coated LWC base paper^v (samples from Table 6).

The felt pen test is considered to give a good preliminary idea of the surface modifying properties of a polymer. The optical images of samples on fine papers are presented in Figure 11 (Optical images were recorded and felt pen tests done by Arto Salminen, Department of Polymer Technology, TKK). Upon treatment of fine papers with PEO homopolymer, the paper surfaces become even more hydrophilic than the untreated paper, as was detected by contact angle measurements.

Figure 11 shows that the ink penetration was stronger in the treated zone (Figure 11 top) than in the untreated zone (Figure 11 bottom). However, when the triblock copolymer (sample 6, Table 6) was sprayed on the paper surface, there was no clear difference in the penetration of the water-based ink in both coated and non-coated areas (data not shown).

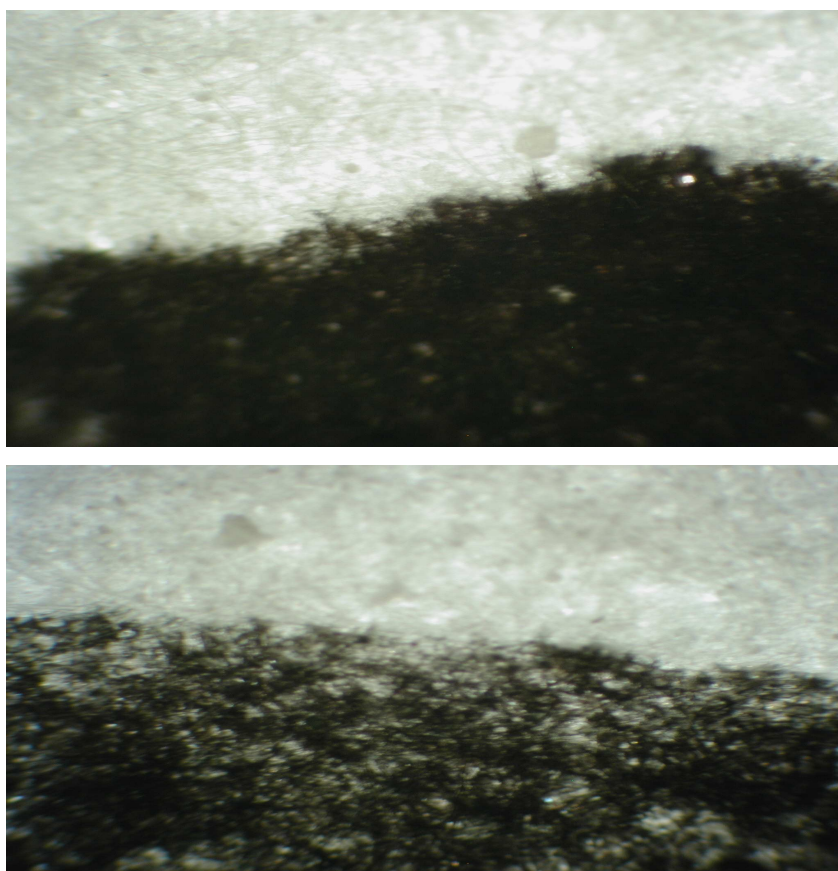


Figure 11. Optical microscope images of felt pen-treated fine paper samples: PEO (20K) (coated) top and non-coated paper below. 2 w-% concentration

Measurements of the absorption of water and oil on the coated paper surface provide additional information about printability. Water and oil absorption measurements were done by Henna Lampinen, VTT. From Figure 12 it can be seen that pure PEO (10 k) polymer increases the rate of water absorption; water wets the PEO-coated surface faster than the non-coated LWC base paper, as measured by parameter AWR, which characterizes wetting of the paper surface in z-direction. AWR is defined as the wetted area divided by the measurement area. When block copolymer containing 5 wt-% PS (sample 5, Table 6) is applied, wetting of the coated surface occurs as fast as in the case of pure PEO. However, when the block copolymer with higher amount of PS (7 wt-%) (sample 6, Table 6) is applied, the rate of water absorption is the same as for the original wood-containing (LWC) base paper.

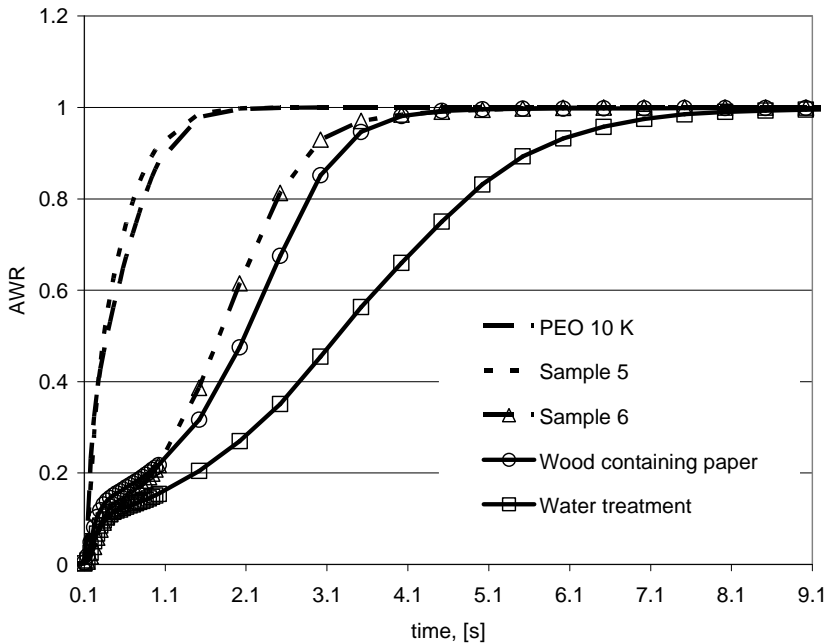


Figure 12. Absorption speed of water in Z-direction as a function of time. Reference samples are wood-containing paper and wood containing paper treated with pure water.^v Sample 5 is PS-b-PEO-b-PS containing 5 wt-% PS and sample 6 is PS-b-PEO-b-PS containing 7 wt-% PS.

3.4.3 Treatment of paper surface with PS-b-PEO-b-PS triblock copolymer containing 10 wt-% PS

In view of the preliminary results reported above, the water-dispersible PS-b-PEO-b-PS triblock copolymer in which PS is 10 wt-% (sample 7, in Table 6) was selected for detailed study of ink penetration and other surface modifications. This polymer is more hydrophobic than the other samples (indicated by contact angle measurements, see below). The penetration of water-based ink was weaker in the coated area than the uncoated area (cellulose fibres of the coated paper were still visible).^v It can be concluded that the penetration of the ink molecules into the paper structure is weakened by the addition of this type of polymer.

Printability was investigated by measurement of water and oil absorption as a function of time. Polarity factors of polymer-coated samples were determined by measuring contact angles with five test liquids (water, ethylene glycol, tricresyl phosphate, formamide, and diiodomethane). Figures 13, 14, and 15 show the results.

Treatment of the surface with PS-b-PEO-b-PS triblock copolymer (sample 7) delayed wetting of the surface with water (parameter AWR) in the case of both fine paper and LWC paper (Figure 13 (a,b)). As to oil absorption, it is clear from Figure 14 (a,b) that coating with polymer (sample 7) did not retard oil wetting of the surface as effectively as water absorption. In general, PS-b-PEO-b-PS triblock copolymer (sample 7) had a greater effect on properties of the LWC base paper properties than on the FP base paper.

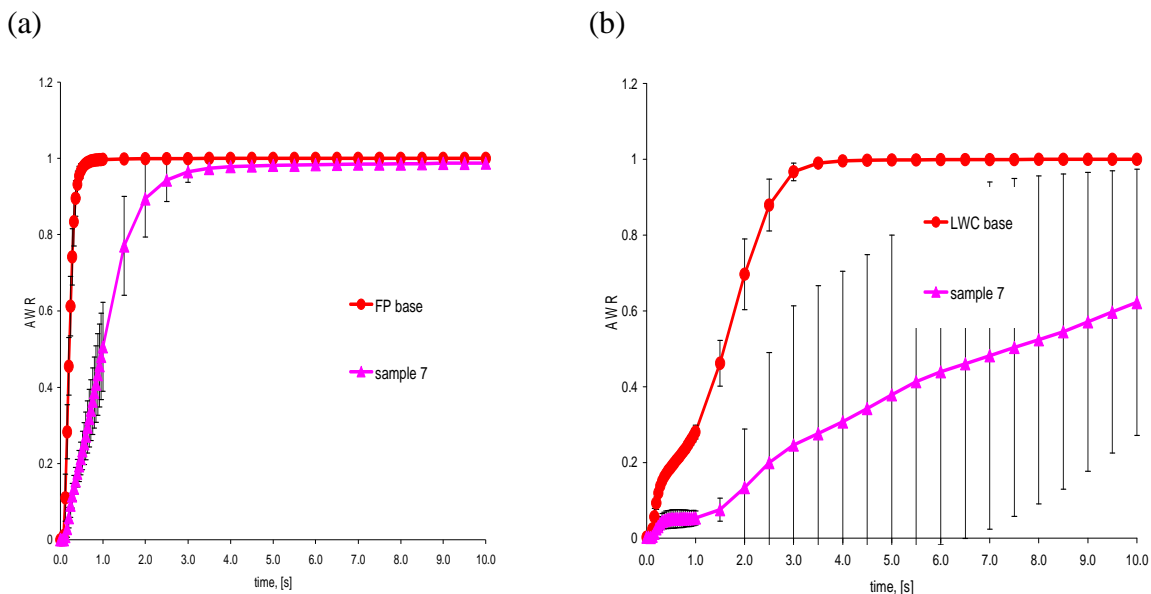


Figure 13. Water absorption measured by parameter AWR of a) fine paper and b) LWC paper as a function of time (sample 7 is PS-*b*-PEO-*b*-PS containing 10 wt-% PS).

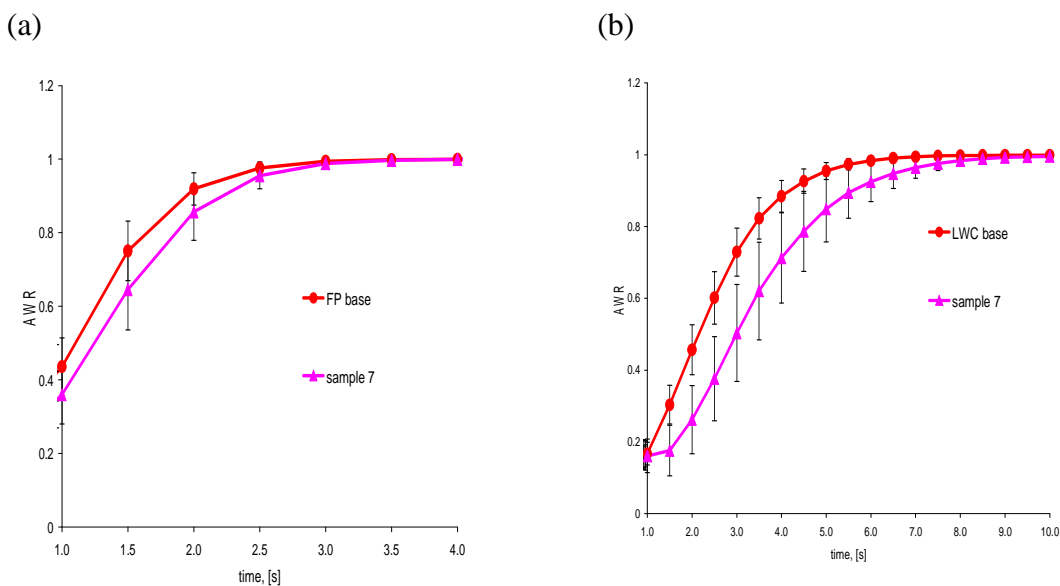


Figure 14. Mineral oil absorption measured by parameter AWR of a) fine paper and b) LWC paper as a function of time (sample 7 is PS-*b*-PEO-*b*-PS containing 10 wt-% PS).

Coating lowered the total surface energy value of the fine paper base (Figure 15 (a)) to almost the same level as that of the fine paper product, but the contact angles of individual model solvents (Figure 15 (c)) differed on the coated and FP product samples. With the FP base paper, sample 7 gave a substantially different value for water than did the FP end product (contact angle for the polymer treated paper $> 115^\circ$ and for the FP end product $< 70^\circ$).

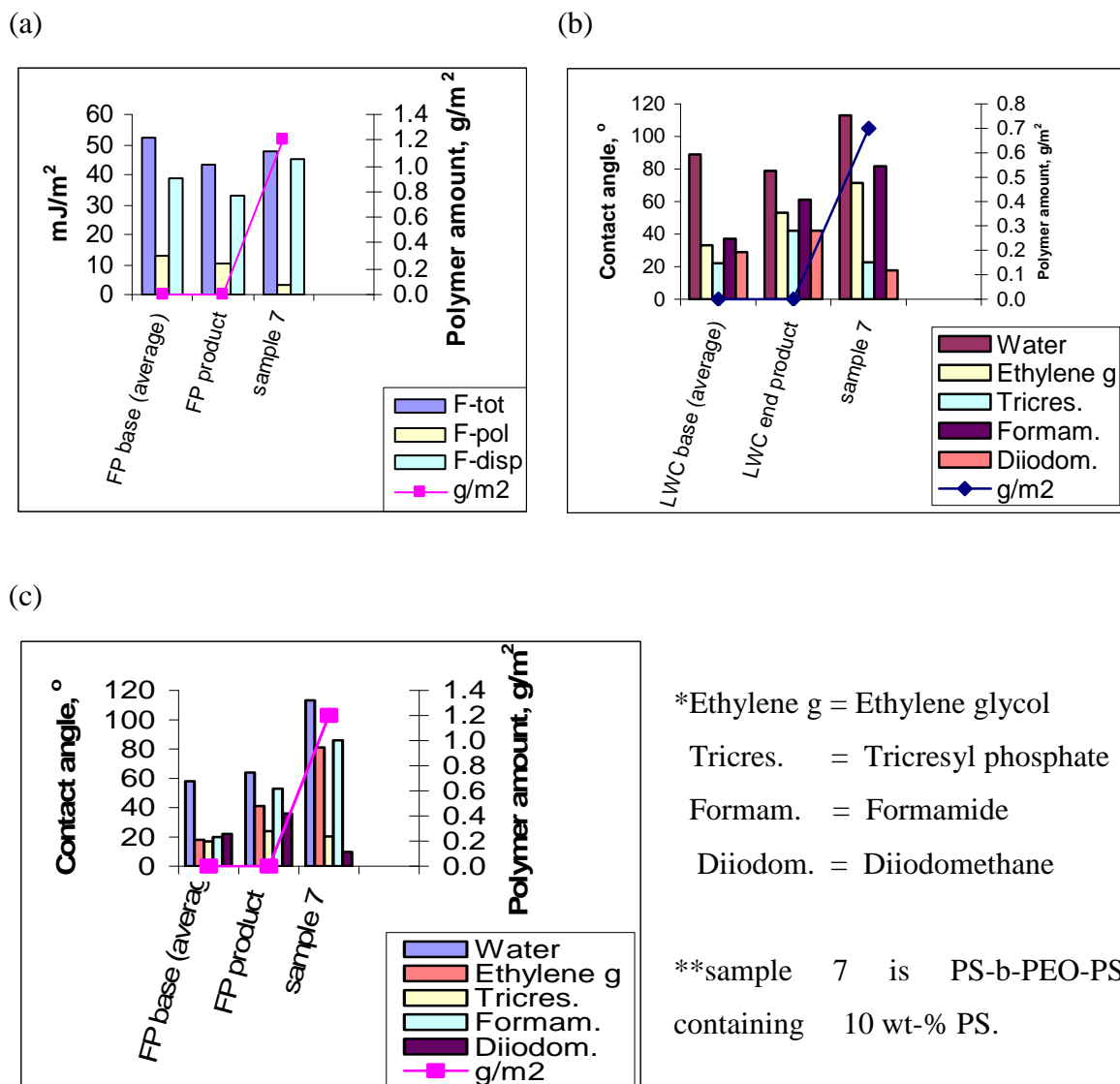
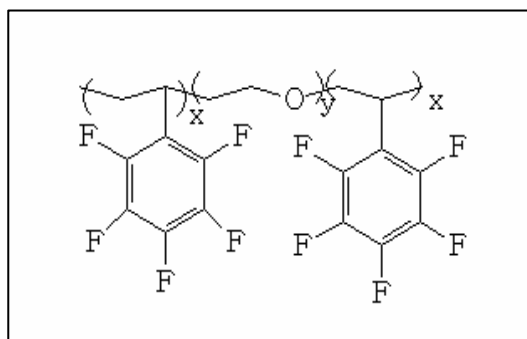


Figure 15. Effect of PS-b-PEO-b-PS triblock copolymer on a) surface energy of FP base paper, b) contact angles of LWC base, papers and c) contact angles of FP base paper.

3.4.4 Treatment paper surface with poly(fluorinated styrene) (PFS-b-PEO) diblock copolymers

Fluorinated block copolymers with well-defined structures can be generated by ATRP. Hvilsted et al.¹⁰⁶ demonstrated fast controlled polymerization of 2,3,4,5,6-pentafluorostyrene (FS) by this technique. Fluoropolymers have attracted significant attention due to their high thermal stability and oil and water repellency. They are extremely hydrophobic materials, exhibiting large contact angle values.¹⁰⁷ An even more hydrophobic surface can be created with fluorinated styrene, than with hydrocarbon styrene.¹⁰⁸

To the best of our knowledge, we are the first to report the synthesis by ATRP of poly(ethylene oxide)-block-poly(2,3,4,5,6-pentafluorostyrene) (PFS-b-PEO) copolymers (di- and triblock structures see for example samples 12 and 13 in Table 6).



Structure of PFS-b-PEO-b-PFS triblock copolymers as prepared by ATRP

Table 8 shows a comparison of contact angles and surface energies of PFS-b-PEO diblock copolymers and their PS-b-PEO counterparts.

Table 8. Contact angles and surface energies of fluorinated styrene polymers. Styrene polymers are included for comparison.

Block structure	Contact angle	Surface energy	wt-%
(M _n ,PEO=5K(g/mol))	at t = 0s		
PFS-b-PEO	90°	41 mJ/m ²	10%-FS
PS-b-PEO	70°	50 mJ/m ²	10%-Styrene

It is clear from the table that polyfluorinated styrenes induce higher contact angles and lower surface energies than non-fluorinated ones. Similarly, Figure 16, which depicts water absorption measurements for PFS-b-PEO and PS-b-PEO polymers on fine base papers, shows fluorinated styrene polymers delay water absorption more than non-fluorinated ones do.

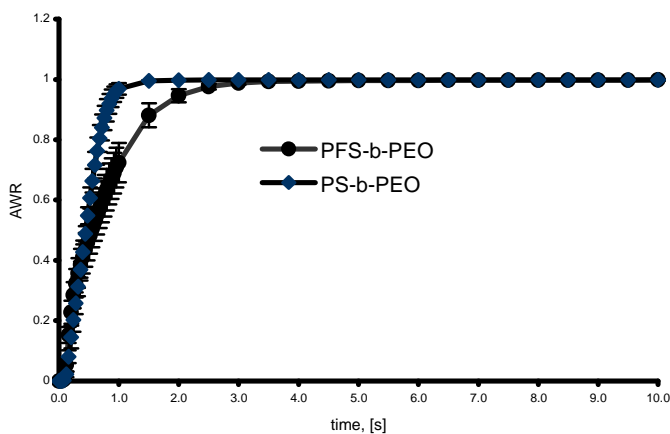
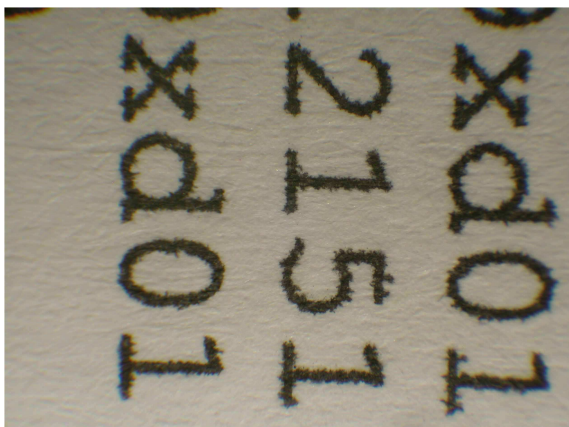


Figure 16. Absorption speed of water in Z-direction of fine paper as a function of time for PFS-b-PEO and PS-b-PEO block copolymers.

It was of interest to perform an ink-jet printing test on base paper coated with PFS-b-PEO polymer. Figure 17 shows that the ink-jet printed text on base paper spray-coated

with polymer PFS-b-PEO is less fuzzy (i.e., sharper edged) than that printed on non-coated base paper or commercial copy paper.

a)



b)

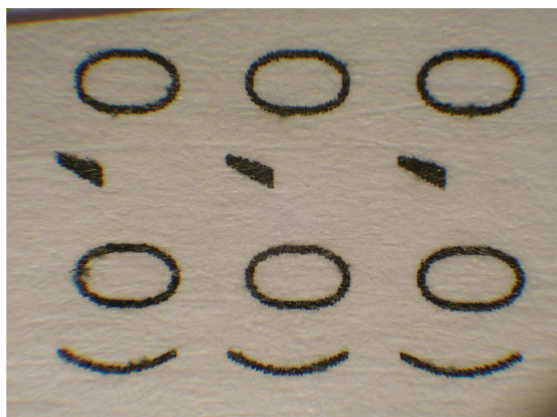


Figure 17. Ink-jet printing text of a) non-coated base paper and b) PFS-b-PEO coated base paper.

4. CONCLUSIONS

The combination of synthetic versatility and simplicity makes ATRP a powerful technique for use in the design and synthesis of new polymeric materials of novel structure. ATRP can be used to polymerize and copolymerize a wide variety of monomers, including styrenes, methacrylates, and acrylates, with accurate control over the molecular weight, molecular weight distribution and composition of the final polymer.

It was demonstrated for four new synthesised tetradentate nitrogen ligands that the rate of polymerization is reduced when steric hindrance is increased on the ligand of iron catalysts. As well as a decrease in the rate there was an associated increase in the molecular weight distribution. Thus the steric effects of the ligands determine the catalyst selectivity and solubility in the reaction mixture. The ligands with significant steric crowding (ligands **2** and **3**) exhibited low reactivity toward halogen abstraction because they form the sterically more demanding Fe(III) species only with difficulty. The catalytic system where the ligand contained a cyclic bridge between nitrogens (ligand **4**) was not active in iron-mediated ATRP.

Amphiphilic diblock and triblock copolymers (PEO-PS and PEO-PMMA-based) with low polydispersities were successfully synthesised by ATRP in bulk using Cl-PEO-Cl or PEO-Cl macroinitiators and CuCl/bipy or FeCl₂·4H₂O/PPh₃ complex as a catalyst. FT-IR and ¹H NMR spectra confirmed the block architecture of the copolymers. The results obtained by GPC analysis confirmed the evolution of the number average molecular weights with monomer conversion and low polydispersities.

Very weak melting and crystallization peaks and no glass transitions of PEO were observed in PMMA-b-PEO-b-PMMA block copolymers, and T_g related to the outer PMMA segments moved to a lower temperature. We suppose that PEO crystallized from a phase-segregated melt into confined microphases in the PMMA matrix.

Water-soluble PEO-PS and PEO-PMMA-based block copolymers were prepared through adjustment of the content of PEO blocks (PEO content >90% by mass). Water-soluble PS-b-PEO-b-PS and PEO-b-PS block copolymers showed promise as coating materials in experiments done on silicon model and paper surfaces. On model silicon surface the diblock structure allowed the formation of more ordered micelle-like particles

whereas the triblock structure led to less ordered aggregates. On the paper surface, PS-b-PEO-b-PS with 7 wt-% PS appeared as the most effective of all synthesised water-soluble block copolymers. The coating hydrophilicity/-phobicity could be modified through change in the PEO/PS ratio in the triblock copolymer. Hydrophobicity of the base paper surface was increased when the paper was coated with copolymer when the molecular weight of PEO block was about 10,000 g/mol and the amount of PS exceeded 7 wt-%. PS-b-PEO-b-PS triblock copolymer containing 10 wt-% PS is a water dispersive-polymer and creates a highly hydrophobic paper surface. It also showed good resistance to water absorption and to a lesser extent to oil absorption. Poly(fluorinated styrene) block copolymers were more hydrophobic and of lower surface energy than with hydrocarbon styrene polymers

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