Atom Transfer Radical Copolymerization of Styrene and Poly(ethylene oxide)-alkyl Methacrylate Macromonomer

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The present paper focuses on the atom transfer radical copolymerization of styrene and an amphiphilic macromonomer poly(ethylene oxide)-alkyl methacrylate (PEOm) which contains a hydrophilic polyethylene oxide segment and a hydrophobic alkyl chain. These block-copolymers were prepared using CuBr/bipy (bipy:2,2'bipyridine) catalyst system in conjunction with ethyl 2-bromoisobutyrate, as initiator, using *o*-xylene as a solvent at 90 ºC. The number-average molecular weights of the resulting block copolymers increased in direct proportion to the monomer conversion and the molecular weight distributions (M_w/M_n) were as low as 1.45. Thus a novel type of block-polymacromonomers with controlled chain lengths for both the backbone and the side chain have been synthesized. The resulting copolymers were characterized by means of room temperature gel permeation chromatograph and ^{1}H NMR spectroscopy, FT-IR spectroscopy and differintial scanning calorimetr.

Key Words: Atom transfer radical copolymerization, Controlled free radical polymerization, Styrene, Block-copolymers.

INTRODUCTION

Design and synthesis of materials with novel properties are becoming an increasingly important aspect of polymer chemistry. Polymers with end-functional groups have attracted considerable attention as prepolymers (macromonomers) for synthesizing block and graft copolymers, star polymers and polymer networks. Macromonomers are usually referred to reactive oligomers or polymers in which a polymerizable functional group is incorporated to the chain end(s). Macromonomers can be synthesized *via* various methods including anionic, cationic, radical polymerizations and chemical modifications of polymer ends[1].

Since its discovery[2-4], atom transfer radical polymerization (ATRP) has proven to be a reliable and a versatile method for synthesis of polymers with narrow molecular weight distributions and controlled structure. Although ATRP has benefited from a huge development over the last years[5-8], only few examples of its use for the homo- and block-(co)polymerization of macromonomers have been described in the literature. Thus far, ATRP has mostly been used for the synthesis of macromonomers and their copolymerization with small monomers[9-11]. ATRP[12-18], were also employed to control the (co)polymerization of macromonomers.

Minoda and co-workers[19] homopolymerized methacryloyl poly(isobutyl vinyl ether) macromonomers *via* ATRP. The macromonomers were synthesized by living cationic polyme-

rization. Atom transfer radical copolymerization of the macromonomers was carried out using CuBr. All the evidences of a controlled polymerization process were observed. Polymacromonomers with a degree of polymerization of up to 200 were obtained for the shortest branches. It is also observed that the polymerization rate decreased with the length of the macromonomers.

It has been recognized that the polymerization of macromonomers is connected with the diffusion and chemical controlled kinetic events. The high segment density, the chain dimensions of macromonomers and/or their coils and polymer chain entaglements differ from those of linear polymer chains. The addition of low molecular weight comonomer is expected to decrease the effect of high segment density and the chain dimensions of macromonomer on the polymerization of macromonomers. When dealing with the polymerization mechanism of macromonomers, a copolymerization system containing the low molecular weight comonomer could be more suitable to follow gradually perturbation in the macromonomer system. For example, the emulsion or dispersion copolymerization which is very closely related to the monomer composition can give useful information which a homopolymerization can not provide.

Tenhu and co-workers[20,21] synthesized an amphiphilic macromonomer (PEOm) that contains a hydrophilic polyethylene oxide (PEO) segment and a hydrophobic alkyl chain.

A reactive methacrylate end group was introduced on the alkyl end. The macromonomer (PEOm) has the following structure

$$CH_3O-[CH_2CH_2O]_{42}-[CH_2]_{11}-O-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{\overset{\displaystyle CH_3}{|}}{C}=CH_2$$
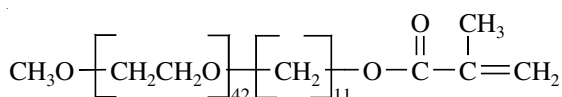
Amphiphilic polymacromonomers and polymers are typical non-ionic polymeric surfactants which have attracted considerable attention because of their outstanding solution properties and a wide range of applications. These materials are very interesting from the point of view of fundamental research, as they exhibit self-assembling properties in the presence of a selective solvent or surface. Earlier[22,23] we reported the ATRP synthesis of amphiphilic polymers and copolymers and their applications as paper coating materials and we still interested in amphiphiles. For the above mentioned reasons, this paper reports on a ATRP copolymerization of styrene and (ethylene oxide)-alkyl methacrylate macromonomer block-copolymerization (PEOm-PS) which were achieved by the macromonomer approach (**Scheme-I**).
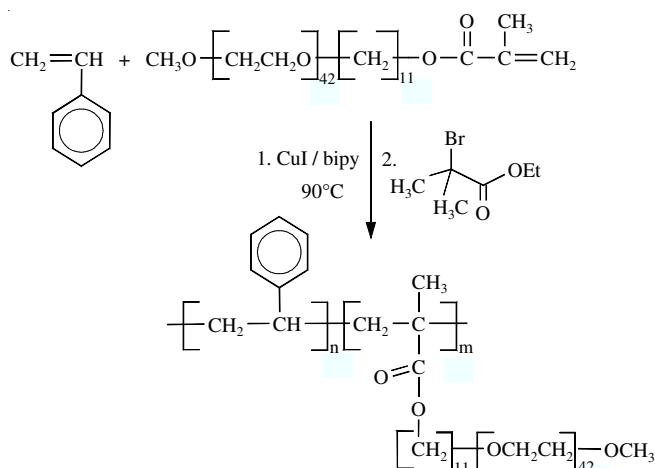
Scheme-I: Copolymerization of styrene and (ethylene oxide)-alkyl methacrylate macromonomer (PEOm-PS) *via* atom transfer radical polymerization

EXPERIMENTAL

The (ethylene oxide)-alkyl methacrylate macromonomer was synthesized, purified and supplied by professor Tenhu[20], (University of Helsinki, Finland) and it was then stored under nitrogen. Styrene (Aldrich, 99 %) was purified by passing it through a column of activated basic alumina to remove inhibitor. It was then stored under nitrogen at -15 ℃. 2,2'-bipyridine (bipy) 99 % (Aldrich) and copper(I)bromide 98 % (Aldrich) were used without purification. Ethyl-2-bromoisobutyrate ((CH_3)_2CBrCO_2Et) (Aldrich, 98 %) was dried under molecular sieves. All solvents were purchased as HPLC grade and dried with molecular sieves or distilled over sodium under argon atmosphere.

Copolymerization of styrene and (ethylene oxide)-alkyl methacrylate macromonomer: In a typical polymerization, a schlenk tube was charged with the macromonomer (0.4 g, 0.189 mmol), CuBr (2.7 mg), bipy (9 mg), styrene (10 mL, 87.1 mmol), *o*-xylene solvent (10 mL). The solution was stirred vigorously until the macromonomer and CuBr were completely dissolved. Finally, the initiator ((CH_3)_2CBrCO_2Et) (3.68 mg, 0.0189 mmol) was added. The tube was sealed and placed in an oil bath at 90 ℃ for a desired time, then the reaction was stopped and the reaction mixture was cooled to room temperature and 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 washed twice with distilled water at room temperature in order to remove possible unreacted PEO macroinitiator and the purified product was dried in vacuum at room temperature and the yield determined gravimetrically.

Characterization: The percentage conversion of the block copolymer was determined by weighing the dried polymer. The molecular weights were determined by room temperature gel permeation chromatograph (GPC) (Waters System Interface model, Waters 510 HPLC Pumps, Waters Differential Refractometer, Waters 700 satellite Wisp and four linear PL gel columns: 10^4, 10^5, 10^3 and 10^2 Å connected in series 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.

The ^{1}H NMR spectra of the polymer were recorded using a Varian Inc. (Palo Alto,CA) Gemini 2000 XL NMR spectrometer operated at 300 MHz. The polymer solution was prepared by dissolving about 50 mg of polymer in 3 mL of CDCl_3.

FT-IR spectra of the macroinitiator and block copolymers were recorded on a Nicolet Impact 400 Fourier Transform Infrared Spectrometer using the KBr pellet technique.

Glass transition temperatures (T_g) were determined with a Perkin-Elmer. DSC 7 differential scanning calorimeter with samples (11-16 mg) prepared from powders and sealed in aluminium pans. The heating rate was 10 ℃/min and liquid nitrogen was used for runs from -60 ℃.

RESULTS AND DISCUSSION

Homopolymerization of PEOm macromonomer: It has been found that the homopolymerization of PEOm macromonomer in the presence of CuBr/bipy is quite difficult to achieve. Only a trace amount of the polymer was obtained after 48 h at 90 ℃ and the molecular weight distribution was greater than 1.5 and the molecular weight was not in agreement with the predetermined one. Therefore the homopolymerization of PEOm macromonomer was not a "living" process. Wang and Huang[24] reported the same findings when they tried the homopolymerization of methacryloyl-terminated PEO macromonomer in the presence of 4-hydroxyl-2,2,6,6-tetramethylpiperidine-1-oxide (HTEMPO).

Controllability of (PEOm-PS) copolymers: Table-1 shows the outcome of the atom transfer radical polymerization copolymerization of styrene and (ethylene oxide) alkyl methacrylate macromonomer (PEOm-PS). The molecular weight of the copolymers increases with the polymerization time, which shows the basic properties of the "living" radical polymerization.

Table-1 also depicts that in the early stage of polymerization the conversion increased rapidly with the time due to the higher monomer concentration and then the increase of the conversion slowed, especially for the macromonomer PEOm, where the increase of the conversion was much slower than that of the styrene. It may be attributed to the high viscosity of the system in the later stage of the reaction leading to the difficulty of diffusing PEOm. This phenomenon is more serious for PEOm than styrene.

TABLE-1
COPOLYMERIZATION DATA FOR PEOm
MACROMONOMER WITH S MONOMER*

Reaction time (h)	M_n (g/mol) ($\times 10^{-4}$)	M_w/M_n	Conversion** (%)	
			PEOm	S
3	0.300	1.33	4.5	3.0
5	0.400	1.45	10.2	8.0
8	0.450	1.35	12.3	10.1
12	0.510	1.30	17.3	15.4
15	0.675	1.49	22.0	18.3
24	1.420	1.45	46.2	42.3
48	1.920	1.49	57.1	55.2

*[S] = 4.33 mol/L. [PEOm] = 9.45×10^{-3} mol/L. [Catalyst]/[Initiator] = 1, **Determined by ^{1}H-NMR.

Table-2 shows the influence of the reaction time on the total conversion of the atom transfer radical polymerization copolymerization of styrene and (ethylene oxide) alkyl methacrylate macromonomer (PEOm-PS). The total conversion was calculated using the following formula:

TABLE-2
CHARACTERISTICS OF PEOm MACROMONOMER AND
PEOm-PS BLOCK COPOLYMERS*

Sample	M_n (GPC)	Time (h)	Total conversion (%)	M_w/M_n
PEOm	4800	–	–	1.13
PEOm-PS1	6750	15	20	1.49
PEOm-PS2	14200	24	44	1.45
PEOm-PS3	19200	48	56	1.49

*Conditions as in Table-1.

Total conversion = (weight of PEOm in copolymer)/(initial weight of PEOm) × (initial molar fraction of PEOm) + (weight of S in copolymer)/(initial weight of S) × (initial molar fraction of S).

From this Table it is obvious that both the molecular weight and the total conversion of the copolymers increase with time. Fig. 1 illustrates a kinetic plot of the total conversion *versus* time, showing that monomer conversion increases with time and that the reaction rate is slow (56 % conversion in 48 h).

Fig. 2 reveals a semi logarithmic plot of the ATRP of the resulting copolymers. The plot of $\ln([M]_0/[M]_t)$ *versus* time (where M_0 = initial concentration of the monomer and M_t = monomer concentration at any time) is linear suggesting a constant number of propagating species throughout the reaction.

Molecular weight distribution (M_w/M_n) is less than 1.5 for all copolymers obtained (Table-2). Moreover, by comparing M_n obtained by GPC with the one obtained by ^{1}H NMR for the synthesized copolymers, it is realized that they are in good agreement (for example, $M_{n(GPC)}$ for PEOm-PS3 (entry 4, Table-2) is 1.9×10^4 g/mol, whereas M_n(^{1}H NMR) for the same sample
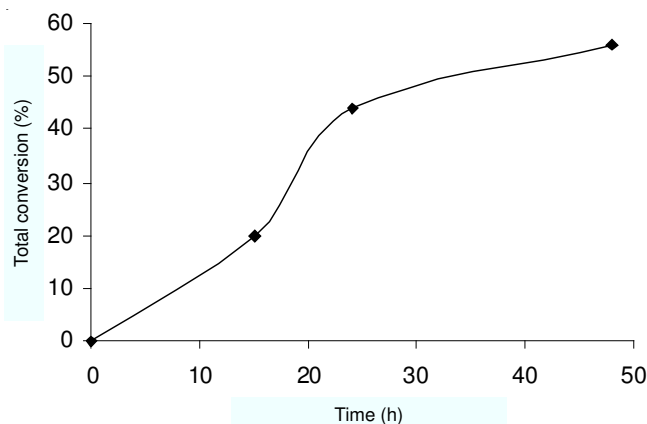

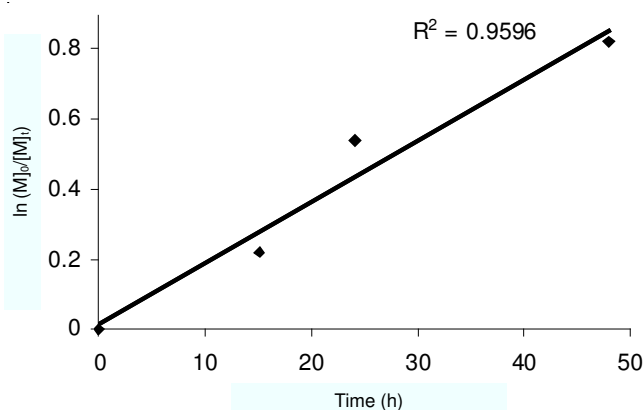Fig. 1.   Total conversion *versus* reaction time in solution using *o*-xylene as a solvent at 90 ºC

Fig. 2.   First order kinetic plot of $\ln([M]_0/[M]_t)$ *versus* time in solution using *o*-xylene as a solvent at 90 ºC

is 1.2×10^4 g/mol). $M_{n(GPC)}$ values were obtained using GPC calibrated with linear polystyrene standards and the slight deviation in molecular weights is thus due to differences in the hydrodynamic volume between macromonomer and linear polystyrene molecules. The above mentioned results show the basic properties of the "living" free radical polymerization.

Gel permeation chromatography curves of the copolymers obtained are presented in Fig. 3. The GPC curves indicate that PEOm-PS block copolymers are formed since the entire elution curves are shifted linearly towards high molecular weights. In addition, the obtained copolymers showed acceptable narrow molecular weight distribution (M_w/M_n) value below 1.5. It is worth noting that GPC trace shows a slight amount of recombination reaction for copolymer 1 (PEOm-PS1, entry 2, Table-2) leading to a small shoulder at relatively low elution volume. This may be attributed to the slow reactivity of high molecular weight macromonomers at the early stage of copolymerization course due to the difficulty of diffusing PEOm macromonomer.

Characterization of (PEOm-PS) copolymers

^{1}H NMR spectra of the (PEOm-PS) copolymers: The macromonomer (PEOm, entry 1, Table-2) was characterized by ^{1}H NMR using chloroform as a reference substance. δ (ppm): 6.1 (1H, HC = C, *trans*), 5.6 (1H, HC = C, *cis*), 4.1 (2H, CH$_2$O), 3.6 (168H, (CH$_2$CH$_2$O)$_{42}$, 3.5 [2H (OCH$_2$(CH$_2$)$_9$], 3.4 (3H, OCH$_3$), 2.0 (3H, CH$_3$C=C), 1.3-1.7 [18H (CH$_2$)$_9$].
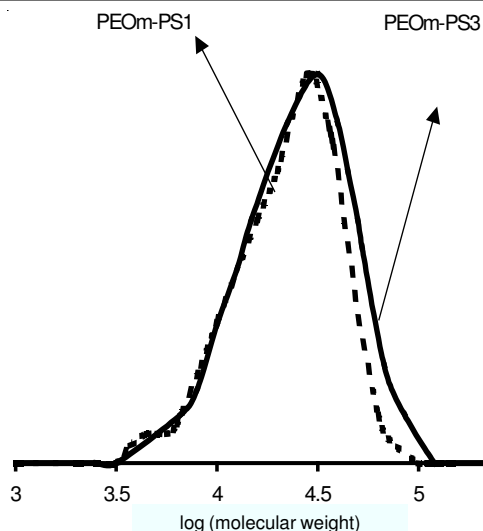
Fig. 3. GPC traces of PEOm-PS block copolymers: PEOm-PS1 (dotted), PEOm-PS3 (solid)

Fig. 4 shows the ^{1}H NMR spectra of the PEOm-PS1 copolymer. The complete substitution of the C=C around 5.6 and 2.0 ppm disappeared after the formation of the (PEOm-PS) copolymers and a new signal at δ = 6.5 and 7.2 for the phenyl ring protons appeared simultaneously. In the ^{1}H NMR spectra, the CH$_2$CH$_2$-O resonance is still observed at 3.6 ppm.
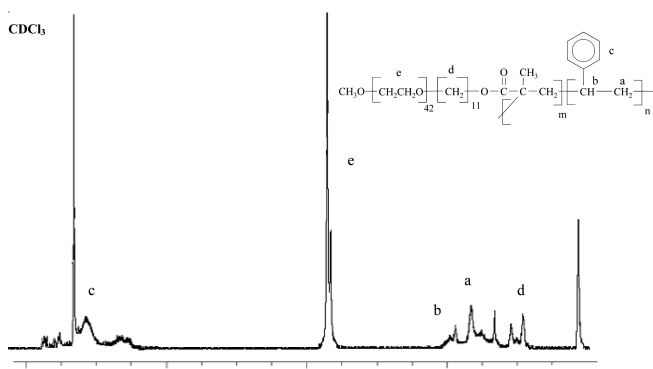

Fig. 4. ^{1}H NMR spectrum (CDCl$_3$) of PEOm-PS1 (Table-1, entry 2)

FT-IR spectra of the (PEOm-PS) copolymers: Representative FT-IR spectra of PEOm macromonomer and PEOm-PS block copolymers are shown in Fig. 5. After the ATRP polymerization reaction, the characteristic bonds of polystyrene at 3100-2900 cm^{-1} were observed. Moreover, the phenyl ring absorption peaks at 750 and 700 cm^{-1} were observed in FT-IR of PEOm-PS.

Analysis of the glass transition temperature: The glass transition temperatures (T$_g$) were measured to check the phase behaviour and the existence of the different blocks in the copolymer. An existence of one or more glass transition temperature is often an argument for discussing whether or not a block copolymer presents one or more phases. A glass transition temperature for the polystyrene segment at about 106 ℃ was found in the differential scanning calorimetry (DSC) of PEOm-PS2 (Fig. 6). In addition, no T$_m$ peaks due to the corresponding macromonomer, PEOm (T$_m$ = at 64 ℃) has been observed. The scan showed a T$_g$ peak which was a bit higher than the
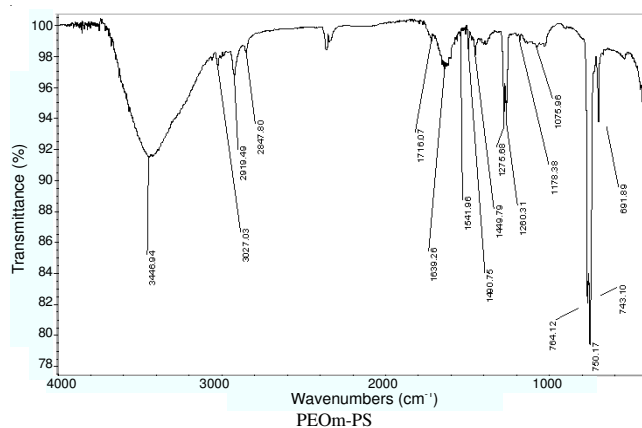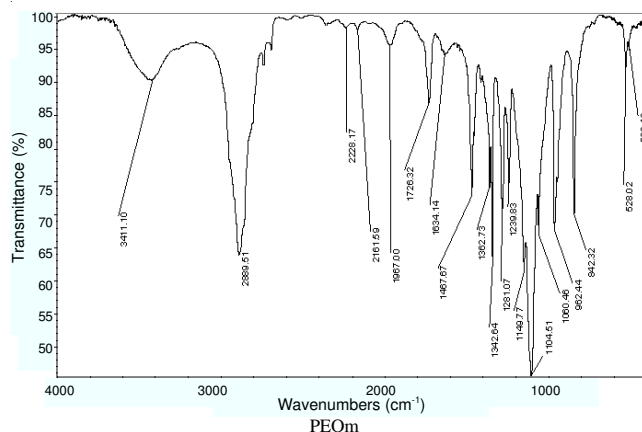

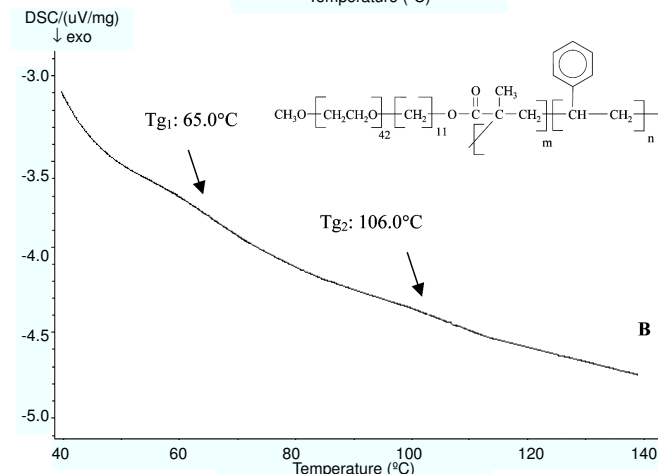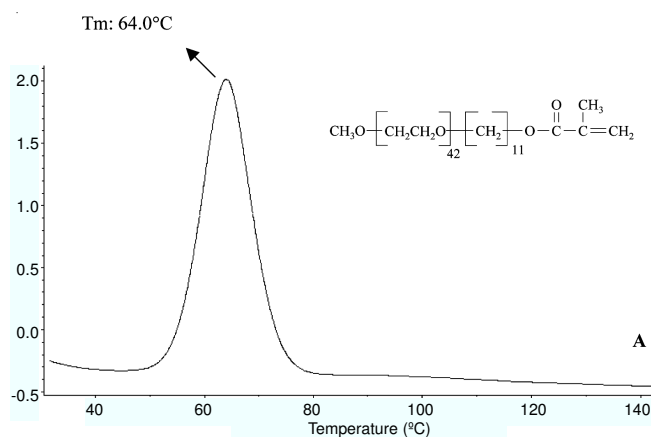Fig. 5. FT-IR spectrum of PEOm and PEOm-PS1 (Table-1, entry 2)

Fig. 6. DSC of (ethylene oxide)-alkyl methacrylate macromonomer (PEOm, A) and PEOm-block-polystyrene copolymer (PEOm-PS2, B)

normal one for homopolystyrene at about 100 ℃. This noticeable shift in the T_g of the blocked polystyrene was attributed to blocking with macromonomer and it confirms the formation of block structure.

Conclusion

The copolymerization of macromonomers with small monomers are generally carried out by a radical method, in which molecular weight and molecular weight distribution of the copolymers are difficult to control. But by applying ATRP technique, block-copolymers of styrene and (ethylene oxide)-alkyl methacrylate macromonomer were successfully polymerized in *o*-xylene solvent using CuBr/bipy catalyst and ethyl 2-bromo isobutyrate as the initiator. It was found that in the preliminary stages the total conversion slowed due to the difficulty of diffusing PEOm macromonomer. GPC, ^{1}H NMR spectroscopy, FT-IR spectroscopy and DSC all these evidences showed that polystyrene had been successfully blocked into the PEOm by the ATRP technique. Solution properties and morphology of this block copolymer will be our next study.

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