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SYNTHESIS OF PS-PEG AND PMMA-PEG BRANCHED BLOCK COPOLYMERS BY MACROINIMERS

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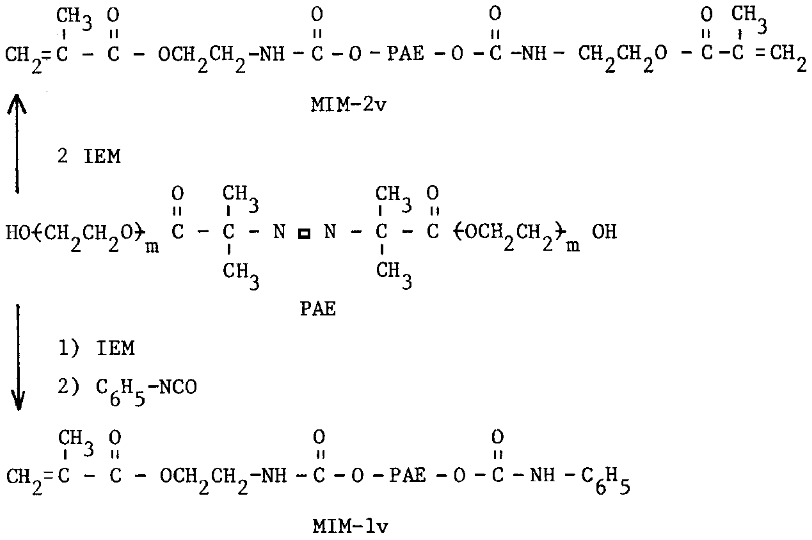
ABSTRACT

A new type of macroinimers were synthesized by the capping reaction of hydroxyl groups of polyazoesters with isocyanatoethyl, methacrylate in the presence of dibutyl tin dilaurate. Macroinimers having PEG-400 and PEG-1500 units were used in the polymerization of methyl methacrylate (MMA) or styrene (S) to obtain PS-PEG or PMMA-PEG branched block copolymers at 60°C. Longer polymerization times or higher macroinimer concentrations led to cross-linked block copolymers. Similarly neat homopolymerization of macroinimers also led to the cross-linked polyethyleneglycols. The products were characterized by IR and NMR spectroscopy, viscosity measurements and fractional precipitation.

INTRODUCTION

Very recently, macro-initiator-monomers (macroinimers) were first described by Hazer[1]. The first type of macroinimer having PEG units was synthesized by the reaction of polyazoesters[2] with methacryloyl or 4-vinyl benzoyl chloride.

The present paper refers to the synthesis of some new macroinimers. Polyazoesters and isocyanato ethyl methacrylate (IEM) were reacted in the presence of dibutyl tin dilaurate (DBTDL) to obtain macroinimer having two vinyl terminal groups (MIM-2v). To obtain macroinimer having a vinyl terminal group, the other hydroxyl end of polyazoester was capped with phenyl isocyanate after the one was capped with IEM (MIM-1 v). The reaction scheme is as follows:



$$CH_2=\overset{CH_3}{\overset{|}{C}} - \overset{O}{\overset{\|}{C}} - OCH_2CH_2-NH-\overset{O}{\overset{\|}{C}}-O-PAE-O-\overset{O}{\overset{\|}{C}}-NH-CH_2CH_2O-\overset{O}{\overset{\|}{C}}-\overset{CH_3}{\overset{|}{C}}=CH_2$$

MIM-2v

2 IEM

$$HO\left(CH_2CH_2O\right)_m\overset{O}{\overset{\|}{C}} - \underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}} - N=N - \underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}} - \overset{O}{\overset{\|}{C}}\left(OCH_2CH_2\right)_m OH$$

PAE

1) IEM

2) C_6H_5-NCO

$$CH_2=\overset{CH_3}{\overset{|}{C}} - \overset{O}{\overset{\|}{C}} - OCH_2CH_2-NH-\overset{O}{\overset{\|}{C}}-O-PAE-O-\overset{O}{\overset{\|}{C}}-NH-C_6H_5$$

MIM-1v

Macroinimers obtained in this work were used in the free radical polymerizations of MMA or styrene to obtaine branched block copolymers.

MATERIALS

Isocyanato ethyl methacrylate (IEM) was a product of Du Pont and it was a gift from Y.Menceloğlu, ITU. Istanbul.

Polyazoesters, PAE-400 and PAE-1500 (molekular weights of PEG units in paranthesis) were prepared by the Pinner synthesis from AIBN and polyethylene glycols (PEG) with molecular weights 400 and 1500 according to Walz et al[2].

Phenyl isocyanate was supplied from Merck, Dibutyl tin dilaurate (DBTDL) was a product of Cincinatti Milacron chemicals. They were used without purification. Methylmethacrylate (MMA) and styrene were purified in a conventional manner.

METHODS

Synthesis of macroinimers: MIM-2v-400 and MIM-2v-1500 in a typical procedure for MIM-2v-400; PAE-400 (5.82 g, 6 m mol), IEM (2.48 g, 16 mmol), p-dihydroxy benzene (0.03 g) in 30 mL $C_2H_4Cl_2$ were mixed under argon in the presence of DBTDL (0.05 g) at room temperature. After nine hours, the solution was concentrated under reduced pressure at 30°C and the residue was precipitated from diethyl ether. The upper phase was decanted and red viscose liquid was dried under vacuum at room temperature for three hours and kept in refrigerator until to be used. MIM-2v-1500 was white solid. Synthesis of macroinimers: MIM-lv-400 and MIM-lv-1500. For MIM-lv-400, PAE-400 (10.34 g, 10 mmol), IEM (1.56 g, 10 mmol), o-dihydroxy benzene (0.03 g) and DBTDL (0.05 g) in $C_2H_4Cl_2$ (30 mL) were mixed under argon at room temperature. After 2 hours, phenyl isocyanate (1.5 g, 13 mmol) in $C_2H_4Cl_2$ (10 mL) was added to the solution and stirred for three hours. The solution was concentrated and the residue was precipitated from diethyl ether. Red viscose liquid was dried under vacuum at room temperature. MIM-lv-1500 was white solid. They were also kept in refrigerator until to be used.

Spectroscopic data confirmed the structures of the macroinimers:

^{1}H-NMR (60 MHz) (CCl_4)
δ 3.7 ppm, singlet (CH_2CH_2O protons)
δ 5.6 and 6.2 ppm, multiplet (vinylic protons)
δ 7.4 ppm (phenyl protons) (for MIM-lv-400 and MIM-lv-1500)
IR (NaCl): Characteristic bands ν_{C-O-C} at 1100 cm^{-1},
$\nu_{C=C}$ at 1620 cm^{-1}, ν_{NH}=3340 cm^{-1} (broad). $\nu_{C_6H_5}$ at 1600 cm^{-1}
for MIM-lv-400 and MIM-lv-1500.

Gelation of macroinimers at 60°C

Bulk homopolymerizations of macroinimer samples (0.5 g) were carried out in pyrex tubes under argon to obtain cross-linked polyethyleneglycol at 60°C. Gelation points were observed by the solidification of macroinimers (MIM-lv-1500 and MIM-2v-1500 were also liquid at 60°C). Gelation times of MIM-2v-400, MIM-2v-1500 and MIM-lv-400 were 4, 24 and 140 minutes, respectively. Gelation of MIM-lv-1500 was not seen overnight at 60°C.

Polymerization of styrene and MMA by macroinmers at 60°C.

In a pyrex tube, in which styrene (or MMA) and a macroinimer were charged separately, argon was purged through a needle into the tube for about one minute. The tightly capped tube was put in an oil bath thermostated at 60°C. After the required time period of polymerization, the tube was quickly cooled and the contents coagulated into methanol. The precipitate was filtered off and dried under vacuum at 30°C. The conditions and results for the preparation of block copolymers were listed in Table 1.

RESULTS AND DISCUSSIONS

Macroinimers having one or two vinyl terminal groups were synthesized and characterized by IR and NMR spectroscopy. Characteristic signals of macroinimers on IR and NMR spectra confirmed their structure.

TABLE 1

Bulk polymerization of styrene and methylmethacrylate by macroinimers at 60°C.

a) Styrene

Run No	Macroinimer Type	Conc.,in wt%	Polym. time,min.	Conv.of monomer,in wt%	η^* dL g^{-1}
1	MIM-1v-400	15.5	188	25	0.32
2		15.4	100	11	0.32
3		20.7	170	23	0.30
4		52.6	72	Gelation	-
5	MIM-1v-1500	12.2	100	1.7	0.51
6		18.5	270	13.0	0.48
7		21.7	280	14.8	0.42
8		27.8	253	13.9	0.52
9		36.0	360	40.0	0.42
b) Methylmethacrylate					
10	MIM-1v-400	14.9	31	11.3	0.72
11		23.1	21	10.7	0.66
12		35.9	11	5.9	0.48
13		30.8	102	Gelation	-
14	MIM-1v-1500	15.6	138	14.1	1.02
15		21.7	60	8.9	0.76
16		35.7	36	9.6	0.65
17		35.7	137	Gelation	-

* in benzene, 30°C.

Gelation times of macroinimers change with their molecular weights and the content of vinyl group. So, decreasing in vinyl group and increasing in the molecular weight of macroinimers made them less reactive.

Macroinimers obtained in this work were used in the polymerization of styrene and MMA to obtain branched block copolymer via free radical mechanism (Table 1). Longer polymerization times and higher concentration of macroinimers cause cross-linked block copolymers which do not dissolve in any solvent. Low branched block copolymers by MIM-2v-400 and MIM-2v-1500 could not obtained in several conditions at 60°C. They gave only cross-linked block copolymers. Therefore it can be said that MIM-1v-400 and MIM-1v-1500 are more suitable than MIM-2v-400 and MIM-2v-1500 to obtain branched PS-PEG and PMMA-PEG block copolymers.

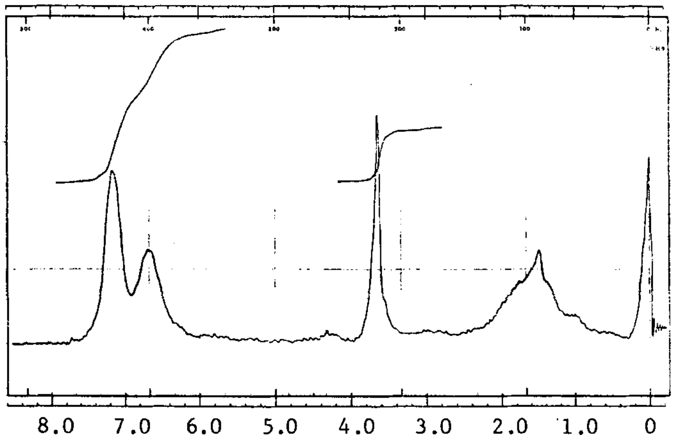


Figure 1. NMR spectrum of PS-PEG block copolymer having 18% PEG (Run no: 1 in Table 1).

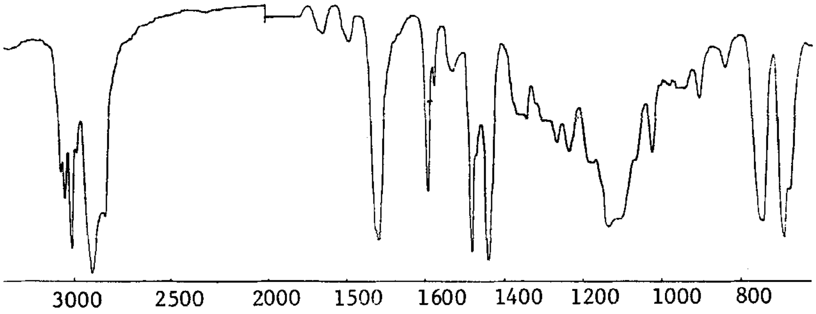


Figure 2. IR spectrum of PS-PEG block copolymer (Run no: 3 in Table 1).

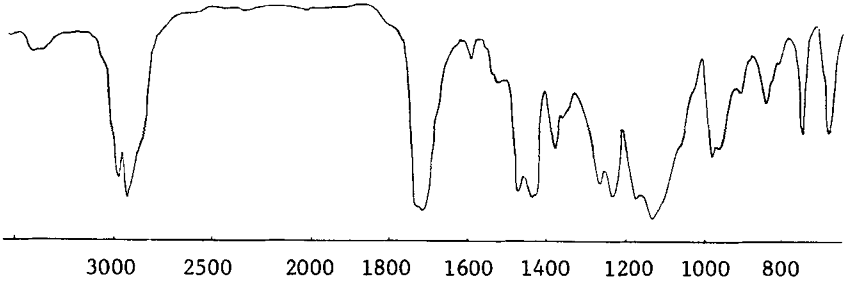


Figure 3. IR spectrum of PMMA-PEG block copolymer (Run no: 8 in Table 1).

A typical NMR spectrum of a PS-PEG block copolymer can be seen in Figure 1. Weight percentage of PEG in PS-PEG block copolymers were calculated from their NMR spectra as 18% for run no: 1 and 15% for run no: 2 in Table 1. IR spectra of PS-PEG and PMMA-PEG block copolymers also confirmed their structure (Figure 2 and Figure 3).

In fractional precipitation, samples were dissolved in THF and precipitated by adding given amount of petroleum ether, gradually. Volume ratio γ of nonsolvent to solvent was 1.4-2.0, when the PS-PEG samples were completely precipitated However, γ for macroinimers and homo-PS were 0.5-07 and 2.5-3.2 respectively. This can be attributed to the block copolymer formation and also decreasing of the solubility of block copolymer because of branching. Similar studies on PEG-PMMA block copolymers were not useful for characterization since their γ values were very close to the related homopolymers (γ for PMMA-PEG: 0.4-0.5, γ for macroinimers: 0.5-0.7 and γ for homo-PMMA: 0.5-0.6).

Highly transparent films of block copolymers which can be attributed to the absence of homopolymer formation, were obtained from their benzene solutions.

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