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Initiation system effects in the cationic copolymerization of tetrahydrofuran (THF)

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Summary

Macromonomeric peroxy initiator, poly tetrahydrofuran (poly-THF=inimer) were synthesized via cationic polymerization of THF by the mono- (*t*-BuBP) and tetra-bromo methyl benzoyl peroxides (BDBP)/$ZnCl_2$ initiating system. The macromonomers were characterized by ^{1}H-NMR, IR, and GPC techniques. Methyl methacrylate (MMA) polymerization initiated by poly-THF inimers at 80°C and different times in bulk gave crosslinked poly-THF-b-polymethyl methacrylate block copolymers. Swelling ratios of the crosslinked block copolymers obtained by taking in same amounts of poly-THF inimer and MMA monomer in $CHCl_3$ were decreased versus time. It was compared the results obtained from *t*-BuBP-, BDBP-$ZnCl_2$ initiating systems with *t*-BuBP-, BDBP-$AgSbF_6$ initiating systems for THF monomer. Poly(THF-b-MMA) crosslinked block copolymers containing undecomposed peroxide groups initiated the thermal polymerization of styrene , S, were used to obtain poly(THF-b-MMA-b-S) crosslinked multicomponent copolymers at 90°C. The crosslinked multi component copolymers were investigated sol-gel analysis and swelling ratios in $CHCl_3$. "Active" poly(THF-b-MMA) having peroxygen group were used in the free radical coupling reaction of poly butadien (Poly Bd). Poly(THF-b-MMA)-polybutadien crosslinked blend soluble graft copolymers were obtained.

Introduction

Macro intermediates such as macroinitiators, macromonomers, and macrocrosslinkers are important in polymer modification leading to block and graft copolymers [1, 2]. Macromonomeric initiators which behave as a macromonomer, macroinitiator, and macrocrosslinker have attracted a great interest because they lead to crosslinked or branched block copolymers. Macroinimers can be divided into two classes, according to the free radical initiator group; (1) macroazo inimers, and (2) macroperoxy inimers. We have recently reported the synthesis of these two types of macroinimers [3, 4]. Poly-THF peroxy inimer as a macroperoxy inimer was previously obtained by the reaction of poly-THF-diol, isophorandiisocyanate, 2,5-dimethyl-2,5-dihydroperoxy hexane, and isocyanatoethyl methacrylate [4, 5]. We have recently described the

synthesis of poly-THF-peroxy inimer obtained by the cationic polymerization of THF with bromomethyl benzoyl *t*-butyl peroxy ester (*t*-BuBP) or bis-(4-bromomethyl benzoyl) peroxide (BBP) or bis-(3,5-dibromomethyl benzoyl) peroxide (BDBP) in the presence of $AgSbF_6$ [6]. Although block and graft copolymers have many similar characteristics, graft copolymer have a branching chain structure attaching polymer units to another polymer backbone [7]. Grafting to the polypropylene, PP, natural rubber, poly butadiene, PBd, and biodegradable natural poly esters, have becoming commercially importance because of their excellent mechanical properties [8].
The present paper describes poly-THF inimer obtained by the cationic polymerization of THF with *t*-BuBP and BDBP in the presence of $ZnCl_2$, copolymerization of MMA with poly-THF inimers at 80°C for 3, 5 ,and 10 hours, the copolymerization of styrene with poly(THF-b-MMA) at 90°C to obtain poly(THF-b-MMA-b-S) multi component copolymer and the grafting reactions of PBd with poly-THF inimers.

Experimental

Materials

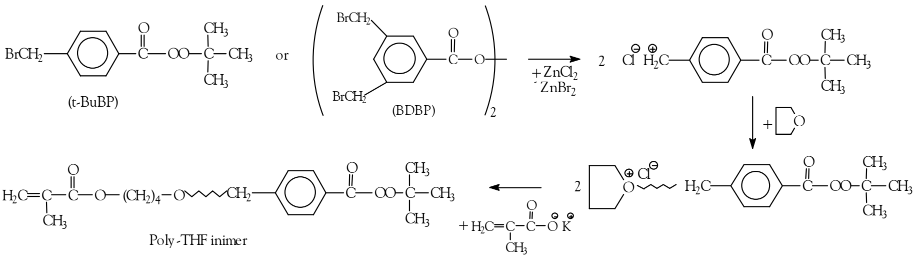
THF was refluxed and distilled over a sodium and benzophenon mixture after producing a purple color, just before use. Styrene was washed with a 10 % aqueous NaOH, water, dried over $CaCl_2$ and CaH_2, respectively, and was then distilled on CaH_2 under reduced pressure before use. MMA was purified in a convertional manner. $ZnCl_2$, PBd were used without further purification. Potassium salt of methacrylic acid was obtained by the reaction of equimolar amounts of methacrylic acid and aqueous KOH solution. It was purified by reprecipitation from methanol solution into excess acetone [9].

Synthesis of bromomethyl functional peroxide initiators (t-BuBP and BDBP)

As a typical example, in order to prepare the mono functional peroxide initiator *t*-BuBP, 4.76 g (21.5 mmol) of 4-bromomethyl benzoyl bromide, 2.4 g (21.5 mmol) of *t*-buthyl hydroperoxide, 10 mL of 30 % aqueous NaOH solution, and 50 mL of diethyl ether were stirred at 0°C for 1 h. Peroxygen analysis were done using potassium iodide and isopropyl alcohol reflux and the sodium thiosulfate titration method [10]. The peroxygen content was found to be 11.1 wt %, in agreement with the theorically calculated value (11.2 wt %). BDBP was synthesized by the procedure reported in [10,11].

Synthesis of poly-THF-inimers

Poly-THF inimers were synthesized by the cationic polymerization between THF (50 mL) initiated by $ZnCl_2$ and *t*-BuBP, BDBP initiator system at 0°C, according to the described procedure [6, 10]. At the end of the given time the potassium methacrylate suspansion of THF was added to the polymerization mixture at 0°C. It was stirred for 3 h, seperated from $ZnBr_2$, (s), and the poly-THF inimer solution was the poured into 0.5 L of cold 0.1 M NH_3 solution. Poly-THF inimer was purified by reprecipitation from diethyl ether solution into petroleum ether (Scheme 1). The results and polymerization conditions are listed in Table 1.



Scheme 1. The reaction of poly-THF inimer.

Table 1. Cationic polymerization of THF with *t*-BuBP, BDBP and $ZnCl_2$ at 0°C

Polymerization system	Run No.	Polymerization time (h)	Conversion, wt %	M_n x 10^{-3}	M_w/M_n
$2x10^{-2}$ M *t*-BuBP+$2x10^{-2}$ M $ZnCl_2$	1	1.5	2.0	1.51	1.06
	2	3.0	2.0	1.90	1.06
	3	6.0	2.5	2.50	1.05
$2x10^{-2}$ M BDBP+$8x10^{-2}$ M $ZnCl_2$	4	1.5	4.0	6.28	1.08
	5	3.0	4.3	7.60	1.06
	6	6.0	4.8	7.95	1.07

Copolymerization of MMA with poly-THF inimer

A given amount of MMA and poly-THF inimer were charged into a pyrex tube. Nitrogen was introduced through a needle into the tube to expel the air. The tightly capped tube was put into an oil bath at 80°C for 3, 5, and 10 hours. Subsequently the reaction mixture was poured into excess methanol to precipitate the block copolymer. Soluble and insoluble fractions were seperated by extracting with chloroform. The swelling ratio, q_V, of the crosslinked block copolymers was calculated by the following equation:

Table 2. Copolymerization of MMA with Poly-THF inimers at 80°C

Run No.	Poly-THF inimer		Monomer MMA(g)	Polym. time (h)	Copolymer yield		Crosslinked Copolymer, wt%	q_v
	Run No.	Amount (g)			g	wt %		
7	1	0.951	0.1004	3	0.262	27.5	60.9	10.30
8	1	0.939	0.1011	5	0.285	30.4	51.9	5.37
9	1	0.919	0.1012	10	0.251	27.3	39.2.	4.93
10	2	0.963	0.1013	3	0.374	38.8	34.8	8.01
11	2	0.960	0.1011	5	0.350	32.9	35.4	5.20
12	2	0.940	0.1014	10	0.345	36.7	44.4	4.53
13	3	0.940	0.1012	3	0.300	28.8	83.5	5.60
14	3	0.946	0.1016	5	0.358	37.8	93.5	3.36
15	3	0.923	0.1013	10	0.649	70.3	99.6	2.98
16	4	0.908	0.1030	3	0.390	38.6	95.0	4.80
17	4	0.937	0.1004	5	0.464	49.5	98.0	3.22
18	4	0.909	0.1026	10	0.637	70.0	99.7	1.96
19	6	0.953	0.1018	3	0.510	53.5	99.8	1.43
20	6	0.900	0.1020	5	0.601	66.7	97.0	1.20
21	6	0.910	0.1017	10	0.800	87.9	98.8	0.98

$$q_v = \frac{V_{\text{dry polymer}} + V_{\text{solvent}}}{V_{\text{dry polymer}}} = \frac{V_{\text{swollen polymer}}}{V_{\text{dry polymer}}}$$

where $V_{\text{dry polymer}}$ and V_{solvent} are the volumes of dry polymer and solvent, respectively. The copolymerization results and conditions are listed in Table 2.

Multicomponent polymerization of styrene with poly(THF-b-MMA)

The crosslinked poly(THF-b-MMA) block copolymers with various compositions were prepared in bulk polymerization at 80°C. In a typical multi component procedure, 0.1 g of poly(THF-b-MMA) block copolymer was swollen in 25 mL styrene at 24 hours. Poly(THF-b-MMA) block copolymer swollen in styrene monomers was kept at 90°C for 8 hours under N_2. Poly(THF-b-MMA-b-S) crosslinked multicomponent polymer samples obtained in this way were seperated from the soluble part soaking in $CHCl_3$. The purified polymer network was dried at 50°C under vacuum for 2 weeks. Table 3 shows reaction conditions and the characteristic data of the multicomponent block copolymers.

Table 3. The copolymerization of styrene with poly (THF-b-MMA) at 90°C

Run No.	Run No. in Table 1.	Poli-THF (g)	Swollen block copolym. in styrene (g)	q_v of block copolym. in styrene	Multi component copolym. yield (g)	Crosslinked multi component copolym. (g)	Crosslinked multi component copolymer yield wt %	q_v of multi component copolym. in $CHCl_3$
25	14	0.1033	0.7938	11.30	0.0989	0.0149	15.1	4.96
26	15	0.1022	0.1142	16.30	0.1415	0.0100	7.1	3.33
27	17	0.1005	0.4138	6.80	0.1588	0.0716	45.1	3.75
28	18	0.1030	0.3609	19.60	0.1816	0.0200	11.1	2.71
29	19	0.1008	0.4876	7.80	0.0728	0.0035	4.8	1.74

Synthesis of p-THF-g-PBd graft copolymer

In a typical grafting procedure, a solution was prepared from a mixture of 0.5 g of poly-THF, 0.5 g of PBd and 30 ml of $CHCl_3$ (as a solvent). The solution was stirred for 24 h, spread on to a glass plate to obtain a polymer film and air-dried. Gel formation was carried out this glass plate by introducing in an oven preheated to 90°C for 6 h. The grafted polymer mixture was extracted with $CHCl_3$ for 24 h. The gels were removed, mixted with methanol and dried in a vacuum oven at 50°C for 2 weeks. The results of grafting procedure are listed in Table 4.

Table 4. Results of the grafting reactions of poly butadiene (PBd) (~0.5g) with poly THF (~0.5g) inimers at 90°C for 6 h

Run No.	Run No. in Table 1.	wt% in the polymer mixture		Grafting copolymer yield, wt%	Crosslinked gtafting polymer yield, wt%	Content of homo PBd, wt %	q_v
		PBd	Poly-THF				
30	1	50	50	89.4	67.7	1.2	8.30
31	4	50	50	84.4	59.1	3.4	6.48
32	6	50	50	74.2	55.0	2.8	4.31

Polymer characterization

^{1}H-NMR spectra were taken on a Varian/Mercury-200 instrument with solvent $CDCl_3$ and tetramethyl silane as the internal standart. IR spectra of the samples were taken on a Perkin Elmer 1600 series FT-IR instrument. GPC chromatograms were taken on a Shimadzu gel permeation chromatograph instrument including a CR-4A chromatopac computer and printer, a CTO-6A colon furnace, an RID-6A detector, and an LC-9A liquid pump. THF was used as a eluant at a flow rate of 0.75 ml/min. A calibration curve was generated with three polystyrene standarts: 250 000, 90 000, 50 000 Daltons, of flow dispersity from Polyscience.

Differential scanning calorimetry (DSC) was performed using a Perkin Elmer 7 series thermal analysis system. Samples were prepared by annealing at 150°C for 5 min. Followed by quenching to -100°C. The heating rate was 20°C/min. Scanning electron micrographs (SEM) were taken on a JEOL JXA-840A electron microscope. The speciments were frozen under liquid nitrogen and were then fractured, mounted, and coated with gold (300 Angstrom) on an Edwards S 150 B sputter coater. SEM measurements were operated at 10 kV and the electron images were recorded directly from the cathode ray tube on a Polaroid film. The magnification employed was varied up to 6000x.

Result and discussion

Mono-, tetra- functional initiators [10, 11] were used in the synthesis of the living poly-THF-containing peroxygen group (active poly-THF), which was terminated by the potassium salt of methacrylic acid to prepare poly-THF inimer. The conditions and results of the polymerization are listed in Table 1. Low conversion of THF between 2.0 and 2.5 wt % for *t*-BuBP, 4.0 and 4.8 wt % for BDBP was observed because bromomethyl initiators are slow initiators in cationic polymerization [12]. This low conversion also helps to keep the solution at a low viscosity to react with methacrylate anion completely. Also for *t*-BuBP/$AgSbF_6$ initiating system, there was no measurable polymer after polymerization for 1.5 h at 0°C, indicating that there is an induction period at around 1.5 h for the monofunctional peroxide initiator system [6]. So it was found that *t*-BuBP/$ZnCl_2$ initiating system is more effective than *t*-BuBP/$AgSbF_6$ initiating system [6]. Number-average molecular weights (M_n) values are determined using both viscosity and gel permeation chromatography (GPC) techniques. M_n values for 1-3 and 4-6 runs in Table 1 increases by increasing of the polymerization time. While the conversion (wt %) in the cationic polymerization of THF with *t*-BuBP in the presence of $AgSbF_6$ were no measurable polymer, 2.9, 3.5 at 1.5, 3.0, and 6.0 hours respectively [6], it was found as 2.0, 2.0, 2.5 for the same times in the cationic polymerization of THF with *t*-BuBP in the presence of $ZnCl_2$. Number-average molecular weights in the cationic polymerization of THF with *t*-BuBP/$ZnCl_2$ initiating system are only bigger in the one half and six hours polymerization time than *t*-BuBP/$AgSbF_6$ initiating system. However it was obtained no measurable polymer with the *t*-BuBP/$AgSbF_6$ initiating system at one half hours. However the conversion obtained with BDBP/$ZnCl_2$ initiating system was generally bigger than its obtained with BDBP/$AgSbF_6$ initiating system and but M_n values of poly-THF inimers obtained with BDBP/$ZnCl_2$ initiating system are smaller than its of BDBP/$AgSbF_6$ initiating system.

Molecular weight distributions were also determined by GPC technique and listed in

Table 1. Molecular weight distrubutions were exchanged between 1.05 and 1.08 in the cationic polymerization of THF with *t*-BuBP and BDBP in the presence $ZnCl_2$, whereas it was exchanged between 1.7 and 3.5 with *t*-BuBP and BDBP initiating system in the presence $AgSbF_6$ [6]. As a result, poly-THF inimers obtained in this work are monodispers. If we compare these values, it can be seen that the M_n of poly-THF inimers increase with increasing initiator functionality. These results are in good agreement with the results obtained by Cai and Yan for cationic polymerization with di-, tri-, and tetra- bromomethyl benzene [13].

The IR spectra of the poly-THF-inimer samples exhibited characterictic peaks at 1740 cm^{-1} (ester carbonyl), 1560 cm^{-1} (vinylic aromatic groups), and 1210 cm^{-1} (etheric groups of poly-THF). The ^1H-NMR spectrum of poly-THF inimer confirms the structural formula in Figure 1. The chemical shifts of the vinylic protons and phenyl protons of poly-THF inimer were observed at 4.6 and 7.4 – 8.2 ppm, respectively.

Copolymerization of MMA with poly-THF inimer demonsrated the macroinimer characteristic behavior [3, 14] resulting in a crosslinked product. The block copolymer yields obtained with *t*-BuBP/$ZnCl_2$ initiating system of MMA has smaller values than BDBP/$ZnCl_2$ initiating system (as shown in Table 2). So it was seen that BDBP/$ZnCl_2$ initiating system is more effective to obtain block copolymer with MMA and has a higher crosslinked block copolymer yield, because BDBP peroxy inimer with tetra-functional group has more vinyl and peroxygen groups than *t*-BuBP peroxy inimer. The 7-9, 10-12, 13-15 runs in Table 2 for poly-THF inimers with *t*-BuBP and the 16-18, 19-21 runs for poly-THF inimers with BDBP show a smooth decrease in q_v, which means the poly-THF inimer obtained after a longer polymerization time (6h) has a smaller q_v (Figure 2). One can conclude that a higher bromomethyl functionality in the peroxidic initiator produces more active cationic sites as the polymerization proceeds [6, 12].

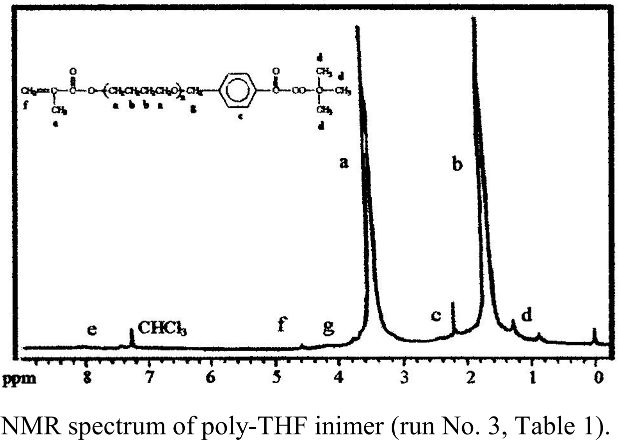


Figure 1. ^1H-NMR spectrum of poly-THF inimer (run No. 3, Table 1).

It was observed that poly(THF-b-MMA) block copolymers obtained by using *t*-BuBP/$AgSbF_6$ initiating system are soluble, but it was obtained insoluble crosslinked block copolymers by using *t*-BuBP/$ZnCl_2$ initiating system. In addition, while the copolymer yield (wt %) and the crosslinked amount (wt %) were taken in the range 30.0-55.6 and 36.5-53.6 respectively, in this work in the range 27.3-87.9 and

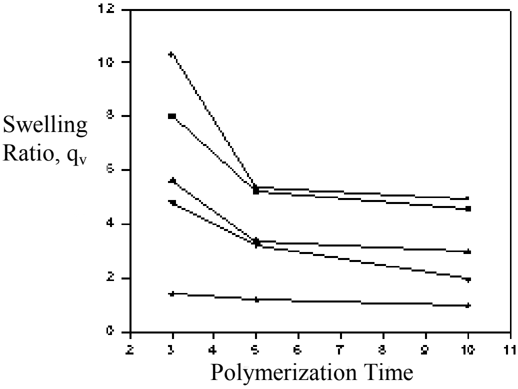


Figure 2. Swelling ratio values of crosslinked poly(THF-b-MMA) block copolymers as a function of polymerization time. (●: run No. 7, 8, 9; ■: run No. 10, 11, 12; ▲ : run No. 13, 14, 15; ▼: run No. 16, 17, 18; ♦: run No. 19, 20, 21 in Table 2).

34.8-98.8. The yields of crosslinked poly(THF-b-MMA) block copolymer obtained with *t*-BuBP/$ZnCl_2$ and BDBP/$ZnCl_2$ initiating systems have higher values than *t*-BuBP/$AgSbF_6$ and BDBP/$AgSbF_6$ initiating systems. It is clear that poly-THF inimers with *t*-BuBP/$ZnCl_2$ and BDBP/$ZnCl_2$ initiating systems are more effective than poly-THF inimers with *t*-BuBP/$AgSbF_6$ and BDBP/$AgSbF_6$ initiating system [6]. When it was compared q_v values, it can be seen that poly(THF-b-MMA) block copolymers obtained with *t*-BuBP/$ZnCl_2$ and BDBP/$ZnCl_2$ initiating systems have smaller q_v values than *t*-BuBP/$AgSbF_6$ and BDBP/$AgSbF_6$ initiating systems, since poly(THF-b-MMA) block copolymers obtained with *t*-BuBP/$ZnCl_2$ and BDBP/$ZnCl_2$ initiating system have higher yield of crosslinked block copolymer [4, 15].

Because the macromonomeric poly-THF inimers contain decomposed peroxygen groups, the graft polymerization of poly-THF inimer with polybutadien was carried out at 90°C. The conditions and the results of the polymerization are listed in Table 4. Thermal analysis of crosslinked block copolymers was carried out by taking DSC curves. All samples exhibited glass (T_g) and melting (T_m) transition arising from the poly-THF units (Figure 3). Peroxygen decomposition of sample 3 in Table 1 around 138 °C was confirmed by the peroxide group in the poly-THF inimer samples.

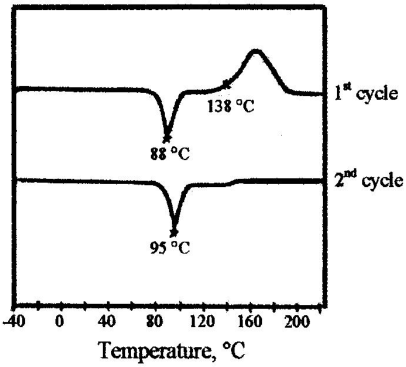


Figure 3. DSC curves of pure poly-THF inimer (run No. 3, Table 1).

Poly-THF units undergo slow crystallization because they have a melting transition around 88-95 °C in the first and even in the second cycle.

Scanning electron microscopy (SEM) micrographs of the samples were used for characterization of the graft copolymer microstructure (Figure 4). For run no. 30, 32 in Table 4, homogenization was not good and grafting of poly-THF units occured only onto the surface layers of PBd. For run no. 31 in Table 4, a good homogenized mixture was obtained in some region of the grafting copolymer but not complete [16].

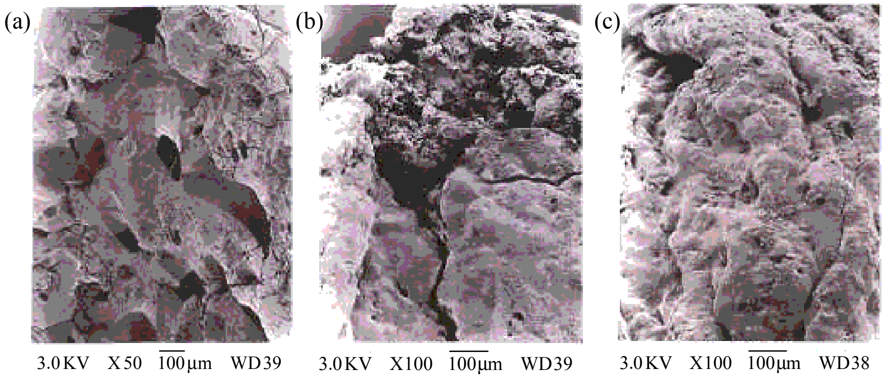


Figure 4. SEM micrographs of graft copolymers in Table 4 (a) run no. 30, (b) run no. 31, (c) run no. 32.

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