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Synthesis of a New Macroperoxy Initiator with Methyl Methacrylate and T-Butyl Peroxy Ester by Atom Transfer Radical Polymerization and Copolymerization with Conventional Vinyl Monomers

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In this study, we present the synthesis of poly-MMA macroperoxy initiators obtained by the ATRP of MMA with bromo methyl benzyl t-butyl peroxy ester (t-BuBP) as an initiator, and CuX (X:Br or Cl)/2,2'-bipyridine (bpy) as a catalyst system at 0, 20, 30 and 40°C. The peroxygen groups do not decompose during the ATRP reaction, because low reaction temperatures used for the ATRP reaction are not enough to decompose them. The peroxygen groups of poly-PMMA macroperoxy initiators can lead them to react with a monomer by using appropriate reaction conditions to obtain the block or graft copolymers. For this purpose, poly-MMA macroperoxy initiators were used to synthesize poly(MMA-b-S) block copolymers with S and used for graft copolymerization of polybutadiene (PBd) and natural rubber (RSS-3) to obtain crosslinked poly(MMA-g-PBd) and poly(MMA-g-RSS-3) graft copolymers. Swelling ratio values of the crosslinked graft copolymers in CHCl₃ were calculated. The characterizations of the polymers were achieved by FT-IR, ¹H-NMR, GPC, DSC, SEM, and the fractional precipitation (γ) techniques. The reaction schemes were also performed using the HYPERCHEM 7.5 program. The mechanical properties of the products were investigated.

Keywords: Atom transfer radical polymerization, free radical polymerization, macroperoxy initiators, block and graft copolymers, mechanical properties, swelling ratio

1. Introduction

When compared with other living radical polymerizations, atom transfer radical polymerization (ATRP) is of great importance due to its many advantages. ATRP works well with a large number of monomers, and offers a more general and efficient way toward various tailor-made polymers (1). ATRP does not require hard conditions and is tolerant of functional groups and impurities (2, 3). Since Matyjaszewski (4) reported the ATRP using alkyl halides as initiators and copper (I) coordinated by a ligand as the catalyst, various monomers have been polymerized in a controlled structure (5–7).

Macrointermediates such as macroinitiators, macromonomers, macrocrosslinkers are important in polymer modification leading to block and graft copolymers (8–18). Macromonomeric initiators which behave as a

macromonomer, macroinitiator, or macrocrosslinker have attracted great interest because they lead to synthesized crosslinked or branched block copolymers. Macroinitiators can be divided into two classes, according to the free radical initiator group: (a) macroazo initiators and (b) macroperoxy initiators (11).

Block copolymers have become increasingly important in recent years (19–21). Recently, block copolymers have been the subject of experimental and theoretical interests due to their practical applications as thermoplastic elastomers (22), superabsorbents (23), unimolecular nanocontainers (24). Free radical polymerization is one of the most important processes for the industrial polymer production, because a broader class of monomers can be polymerized under simple experimental conditions (25). Polymers containing labile azo and/or peroxide groups can initiate vinyl polymerization to obtain block copolymers (26–30).

In recent years, graft polymers have attracted much scientific and industrial interest (31, 32). By using functional polymers containing appropriate alkyl halide and ether groups along the backbone as a macroinitiator, it is possible to obtain graft copolymers in a well-controlled fashion.

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Grafting to the polybutadiene (PBd), natural rubber (RSS-3), natural polypropylene (PP), and biodegradable natural polyesters have become important in widespread use because of their excellent mechanical properties (33).

In this study, the ATRP of methyl methacrylate (MMA) was performed with *t*-butyl peroxy ester (*t*-BuBP) as an initiator, and CuX (X:Br or Cl)/2,2'-bipyridine (bpy) as a catalyst system at 0, 20, 30 and 40°C to obtain the poly-MMA macroperoxy initiators. The peroxygen groups do not decompose during the ATRP reaction, because low reaction temperatures used for the ATRP reaction are not enough to decompose them. The peroxygen groups of poly-MMA macroperoxy initiators can lead to react with a monomer by using appropriate reaction conditions to obtain the block or the graft copolymers. For this purpose, poly-MMA initiators were used to synthesize poly (MMA-*b*-S) block copolymers with styrene (S). We then synthesized poly(MMA-*g*-PBd) and poly(MMA-*g*-RSS-3) graft copolymers by the copolymerization of poly-MMA initiators with PBd and RSS-3. Moreover, we investigated the mechanical properties of the polymers. Several attempts have been made to improve the physical properties and processability of poly-MMA through several procedures in this study.

2. Experimental

2.1. Materials

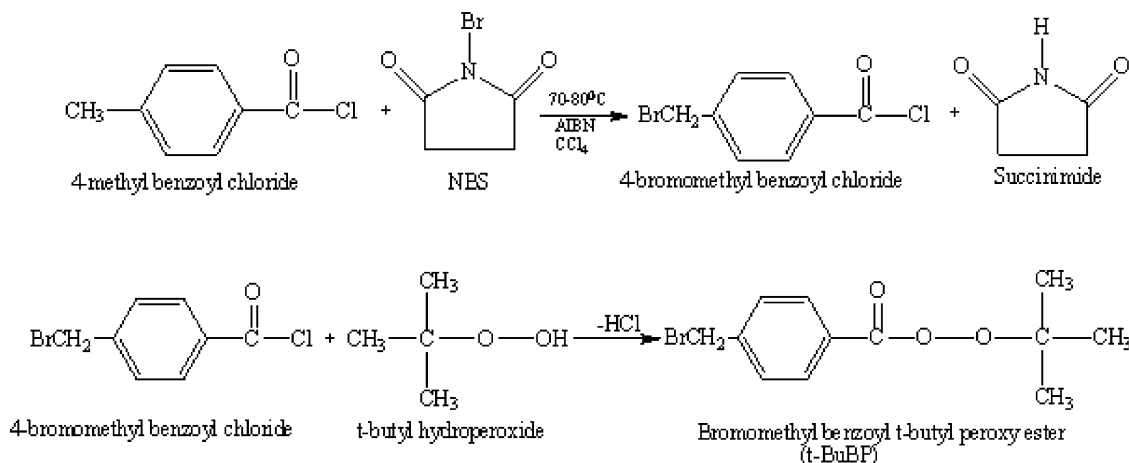
4-methylbenzoylchloride, CuBr, CuCl, and bpy were supplied from Merck and used as received. N-bromo succinimide (NBS) was supplied from Aldrich and used as received. 4-bromomethyl benzoyl chloride was synthesized from 4-methyl benzoyl chloride reacted with NBS (11). S and MMA were supplied from Merck and washed with 10% aqueous NaOH, water dried over CaCl₂, respectively, and was then distilled on CaH₂ under reduced pressure before use. All other chemicals were reagent grade and used as received.

2.2. Polymer characterization

Molecular weights and molecular weight distributions were measured with a Knauer gel permeation chromatograph using ChromGate software, a WellChrom Interface Box, RI Detector K-2301, and WellChrom HPLC pump K-501. CHCl₃ was used as an eluent at a flow rate of 1 mL/min. A calibration curve was generated with six polystyrene standards: 2500, 2950, 5050, 20000, 52000, and 96400 Da, of low dispersity purchased from Polyscience. DSC measurement was carried out under nitrogen by using a Setaram DSC-141 series thermal analysis system. A dried sample was heated at a rate of 10°C/min from -50°C to 120°C under N₂ atmosphere. FT-IR spectra were recorded using a Perkin-Elmer 1600 Series FT-IR Spectrometer. ¹H-NMR of the products was recorded using a Varian/Mercury-200 NMR Spectrometer, in CDCl₃ solvent and tetra methyl silane as the internal standard. The mechanical properties of the polymer samples were measured on a Zwick Z020 tester at room temperature with a crosshead speed of 10 mm/min. SEM was taken on a Jeol JXA-840A electron microscope. The specimens were frozen under liquid nitrogen, then fractured, mounted, and coated with gold (300 Angstrom) on an Edwards S 150 B sputter coater. SEM measurements were operated at 10 kV. The electron images were recorded directly from the cathode ray tube onto Polaroid® film. The reaction mechanisms were performed using the HYPERCHEM 7.5 program (34) on an IBM PC Pentium-IV computer. The optimized geometry was performed using the HYPERCHEM 7.5 parameters for the MM2(MM+) (35).

2.3. Synthesis of *t*-butyl peroxy ester initiator

The mono functional bromomethyl benzoyl *t*-butyl peroxy ester (*t*-BuBP) was synthesized by the reaction of the corresponding bromomethyl benzoyl chloride with peroxides as in the literature (11, 36). Scheme 1 shows the reaction chart for *t*-BuBP. Peroxygen analysis was done using potassium

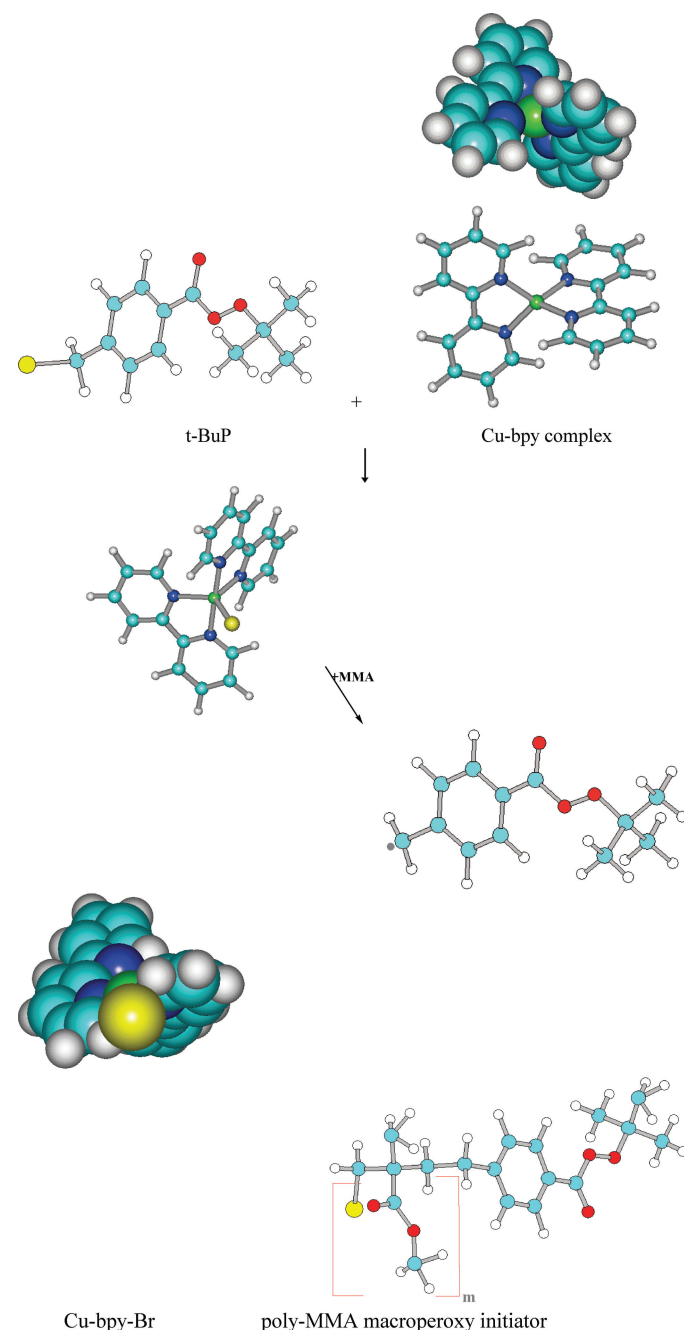


Sch. 1. The reaction pathway of *t*-BuBP.

iodide and isopropyl alcohol reflux and the sodium thio-sulfate titration method (37). The peroxygen content was found to be 10.70%, in agreement with the calculated value (11.20%).

2.4. ATRP Reactions of MMA with *t*-BuBP

0.980 g (3.5 mmol) initiator (*t*-BuBP), 1.640 g (10.5 mmol) ligand (bpy), and 23.4 g monomer (MMA) were added to the flask in a Schlenk system, respectively. The flask was then immersed in a bath at the required temperature. One



Sch. 2. Reaction pathway of poly-MMA macroperoxy initiator with Cu-bpy.

hour of vacuum-nitrogen was applied in order to remove oxygen, and then a catalyst [0.490 g (3.5 mmol) CuBr or 0.338 g (3.5 mmol) CuCl] was added to the solution. After a specific time, the flask was opened and the sample was poured into excess methanol to precipitate the polymer. The obtained polymer was dissolved into chloroform and the insoluble part of the polymer was separated. Poly-MMA macroperoxy initiator was purified by precipitation from diethyl ether:petroleum ether (1:1) solution at room temperature and dried under vacuum to a constant weight. The dried polymer was dissolved in THF and passed through a small neutral alumina column to remove the remaining copper catalyst. The purified macroperoxy initiator was dried at 20°C under vacuum for three days. The reaction pathway may be represented as shown in Scheme 2.

2.5. Copolymerization of S with poly-MMA macroperoxy initiators

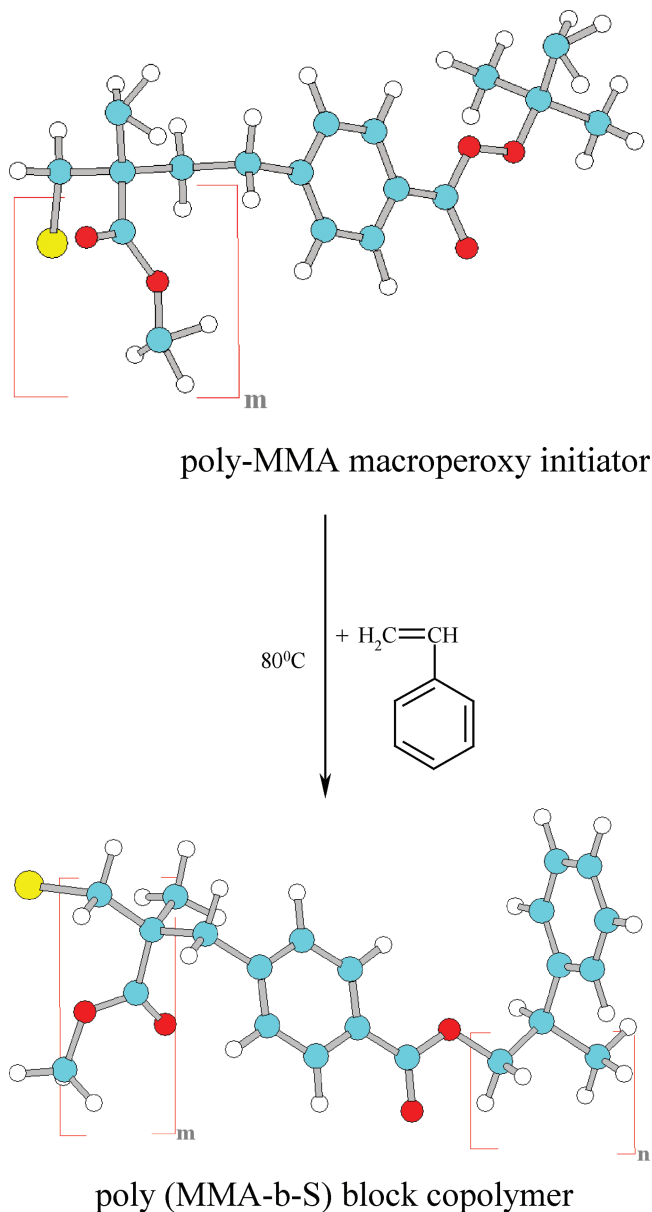
Copolymerization of the S was carried out in bulk. S and the poly-MMA macroperoxy initiator were charged separately into a Pyrex tube, and then nitrogen was purged into the tube through a needle. The tube tightly capped with a rubber septum was put into an oil bath thermostated at 80°C. After the required period of polymerization, the reaction mixture was poured into excess methanol to separate the poly(MMA-*b*-S) block copolymer. The polymer yield was determined gravimetrically. The reaction chart may be seen in Scheme 3.

2.6. Synthesis of poly (MMA-*g*-PBd) and poly (MMA-*g*-RSS-3) graft copolymers

As a typical procedure: 0.1 g of the poly-MMA macroperoxy initiator, 0.1 g of PBd, and 30 mL of CHCl₃ as solvent were stirred for 24 h at room temperature. This solution was spread on a glass plate and dried in the air at room temperature for 2 days to obtain a polymer film; after drying, the polymer film was put into a Pyrex tube. Then, the polymerization was carried out in an oil bath at 90°C under N₂. The graft copolymer mixture was extracted with CHCl₃ for 24 h, so swollen graft copolymer was obtained. The swollen gels were filtered off and mixed with methanol. Then, the poly(MMA-*g*-PBd) graft copolymer was dried under vacuum at 50°C for a week. The same grafting procedure was carried out with the RSS-3 to obtain poly(MMA-*g*-RSS-3) graft copolymer.

2.7. Swelling ratio (q_v) of the crosslinked graft copolymers

The swelling of the crosslinked graft copolymers was carried out by storing 0.2 g of the samples in 50 mL of CHCl₃ for 24 h at 20°C. The swelling ratios (q_v) of the crosslinked



Sch. 3. Free radical polymerization reaction of S with poly-MMA macroperoxy initiator.

graft copolymers were calculated by Equation 1:

$$q_v = \frac{V_{\text{dry polymer}} + V_{\text{solvent}}}{V_{\text{dry polymer}}} = \frac{V_{\text{swollen polymer}}}{V_{\text{dry polymer}}} \quad (1)$$

where $V_{\text{dry polymer}}$ and V_{solvent} are the volumes of dry polymer and solvent, respectively.

3. Results and discussion

3.1. Synthesis of poly-MMA macroperoxy initiators

MMA polymerization was performed using a catalyst mixture composed of the bromomethyl derivative of benzoyl peroxide, CuX (X:Cl or Br), and bpy. t-BuBP leads

to the linear poly-MMA by ATRP reaction. Poly-MMA macroperoxy was soluble in common solvents when compared to t-BuBP obtained from t-butyl hydroperoxide. As a result of the ATRP of t-BuBP with MMA, one-armed poly-MMA initiators were obtained. The monomer conversion was calculated from the weight of recovered polymer. The results and conditions of MMA polymerization are listed in Table 1. According to Table 1, we see that the higher temperature and the longer polymerization times gave the higher molecular weights and the higher yields as expected. High conversion of MMA was observed because bromomethyl initiators were fast initiators in ATRP. The number average molecular weight ($M_{n,\text{GPC}}$) and conversion (wt%) values of poly-MMA initiators synthesized in the presence of CuCl were bigger than those in the presence of CuBr. Molecular weight distribution values of poly-MMA initiators were between 1.25 and 1.61. Molar masses of poly-MMA with a peroxide group in the middle varied from 3,860 to 38,963. The initiator efficiency of poly-MMA initiators was between 0.08 and 0.61, as shown in Table 1.

Based on the assumption that one molecule of t-BuBP initiator generated one polymer chain, the theoretical molecular weight ($M_{n,\text{cal}}$) for ATRP was calculated according to Equation 2 (38), where $[M]_0$ and $[t\text{-BuBP}]_0$ represent the initial concentrations of the monomer and t-BuBP initiator, $(MW)_0$ is the molecular weight of the monomer and 287 is the molecular weight of t-BuBP.

$$M_{n,\text{cal}} = 287 + \{([M]_0/[t\text{-BuBP}]_0)\} \times (MW)_0 \times \text{conversion} \quad (2)$$

3.2. Synthesis of Poly (MMA-b-S) block copolymers

The poly-MMA macroperoxy initiators containing the active peroxide group in the middle were used in S polymerization by thermal free radical polymerization at 80°C to obtain poly (MMA-b-S) block copolymers. The poly-MMA macroperoxy initiators showed the characteristic macroinitiator behavior in the copolymerization of S (14, 29, 30). Table 2 shows the conditions and the results of the polymerization. Molar masses of poly (MMA-b-S) block copolymers were higher than that of the corresponding macroperoxy poly-MMA. Increases in the molecular weights of the products when compared with the macroperoxy initiators confirmed block copolymer formation. Block copolymers purified by fractional precipitation indicated polydispersity values between 1.28 and 2.32 and unimodal GPC curves. The poly (MMA-b-S) block copolymers had high polydispersities because of fast, irreversible termination of the growing radicals through coupling and disproportionation reactions. The polydispersity ratio of poly-MMA used as macroinitiator was between 1.25 and 1.61. Furthermore, this value also affected the polydispersities of the block copolymers.

Table 1. ATRP reactions of MMA with t-BuBP/CuCl or CuBr/bpy initiating system

Run No	Temp. (°C)	Time (hour)	Yield (g)	Conv. (wt%)	$\overline{M}_{n, th}$	$\overline{M}_{n, GPC}$	$\overline{M}_w/\overline{M}_n$	f (initiator efficiency) $\overline{M}_{n, th}/\overline{M}_{n, GPC}$
1 ^a	0	24	3.735	15.96	1,354	7,338	1.32	0.18
2 ^a	20	96	6.453	27.57	2,130	13,450	1.28	0.16
3 ^a	30	96	8.827	37.72	2,809	28,088	1.25	0.10
4 ^a	40	96	10.326	44.13	3,238	38,963	1.61	0.08
5 ^b	0	24	7.242	30.95	2,357	3,860	1.54	0.61
6 ^b	20	72	13.506	57.72	4,147	8,190	1.31	0.51
7 ^b	30	72	19.834	84.76	5,955	11,612	1.47	0.51
8 ^b	40	72	22.376	95.62	6,681	13,165	1.47	0.51

^afor CuCl/bpy initiating system.

^bfor CuBr/bpy initiating system.

CuBr = 3.5×10^{-3} mol, CuCl = 3.5×10^{-3} mol, t-BuBP = 3.5×10^{-3} mol, bpy = 10.5×10^{-3} mol, MMA = 2.34×10^{-1} mol.

3.3. Synthesis of graft copolymerization

Because the poly-MMA macroperoxy initiators contained decomposed peroxygen groups, the graft polymerization of PBd and RSS-3 with poly-MMA initiators was carried out at 90°C. In this process, the poly-MMA macroperoxy initiator was used as radical generators in grafting polymerization. The conditions and the results of the grafting polymerization are in Tables 3 and 4. The poly (MMA-g-PBd) and the poly(MMA-g-RSS-3) films were highly transparent, strong and brittle. Crosslinked and soluble graft copolymer fractions were isolated by means of chloroform extraction for 24 h. After extraction with a suitable solvent, crosslinked copolymer films did not give a considerable soluble part which could be the homopolymer. The q_v value of the graft copolymers decreases while the graft copolymer-

ization conversion increases. Also, the q_v values decrease as the polymerization time increases. Graft copolymers have a branching chain structure attaching polymer units to another polymer backbone (17). In the case of grafting reactions with active poly-MMA, the total polymer yield of crosslinked poly (MMA-g-PBd) and poly (MMA-g-PBd) graft polymers varied from 50.50 to 82.35 wt% and 46.53 to 67.16 wt%, respectively. The swelling ratios of crosslinked graft copolymers varied from 3.16 to 11.22, which can be attributed to a large network structure.

3.4. Characterization of the polymers

The ¹H-NMR spectrum of the poly-MMA macroperoxy initiator (Fig. 1) shows the 0.8 ppm for -CH₃ protons of

Table 2. Free radical polymerization of S using poly-MMA macroperoxy initiator at 80°C

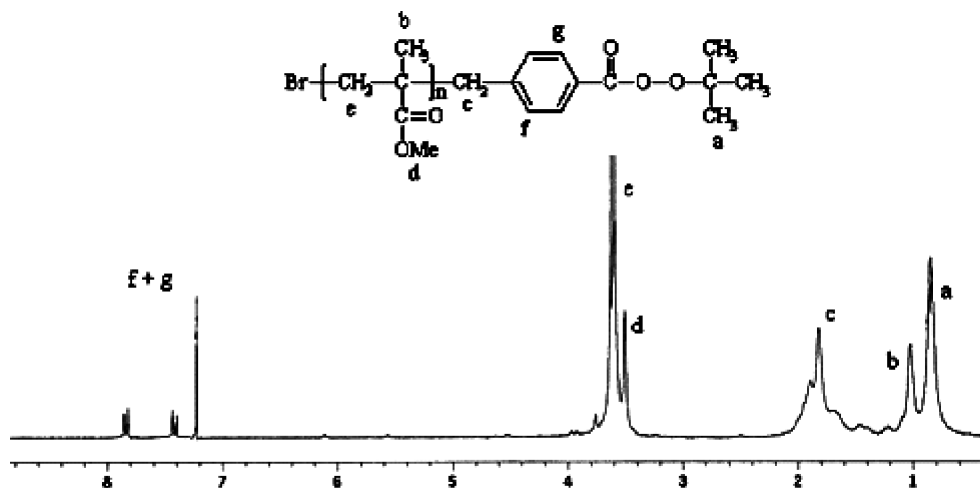
Run No	Time (hour)	Poly-MMA initiator (g)	S (g)	Yield (g)	Conv. (wt%)	γ	\overline{M}_n	$\overline{M}_w/\overline{M}_n$
9	1	0.300(Run no 2 in Table 1)	0.901	0.211	17.56	1.58	22,888	2.04
10	2	0.302(Run no 2 in Table 1)	0.904	0.222	18.41	1.44	22,276	2.17
11	3	0.303(Run no 2 in Table 1)	0.907	0.246	20.33	1.38	23,621	1.93
12	4	0.302(Run no 2 in Table 1)	0.902	0.270	22.43	1.64	24,023	1.98
13	5	0.300(Run no 2 in Table 1)	0.902	0.300	24.96	1.68	21,748	1.96
14	6	0.300(Run no 2 in Table 1)	0.904	0.339	28.16	1.55	23,736	2.01
15	7	0.300(Run no 2 in Table 1)	0.901	0.355	29.56	1.76	19,128	2.32
16	8	0.300(Run no 2 in Table 1)	0.903	0.393	32.67	1.58	22,939	2.12
17	10	0.301(Run no 2 in Table 1)	0.904	0.402	33.36	1.44	22,646	2.21
18	12	0.301(Run no 2 in Table 1)	0.905	0.411	34.08	1.64	23,619	2.02
19	1	0.302(Run no 6 in Table 1)	0.907	0.168	13.73	1.66	10,322	1.40
20	2	0.302(Run no 6 in Table 1)	0.904	0.191	15.84	1.52	10,747	1.43
21	3	0.300(Run no 6 in Table 1)	0.904	0.203	16.86	1.88	10,649	1.39
22	4	0.302(Run no 6 in Table 1)	0.900	0.237	19.72	1.72	12,333	1.39
23	5	0.302(Run no 6 in Table 1)	0.903	0.264	21.91	1.80	10,394	1.28
24	6	0.301(Run no 6 in Table 1)	0.907	0.301	24.92	1.66	13,709	1.37
25	7	0.301(Run no 6 in Table 1)	0.902	0.367	30.51	1.80	11,985	1.43
26	8	0.301(Run no 6 in Table 1)	0.900	0.385	31.98	1.86	12,054	1.39
27	10	0.302(Run no 6 in Table 1)	0.902	0.412	34.22	1.74	14,185	1.36
28	12	0.301(Run no 6 in Table 1)	0.905	0.424	35.16	1.52	13,505	1.38

Table 3. Graft copolymers of PBd with poly-MMA macroperoxy initiator at 90°C

Run No	Time (hour)	Poly-MMA initiator (g)	PBd (g)	Yield (g)	Yield of Crosslinked Graft Polymer (g)		
					g	Con. (wt%)	q_v (in CH_3Cl)
29	4	0.101(Run no 2 in Table 1)	0.102	0.169	0.142	69.95	8.64
30	6	0.102(Run no 2 in Table 1)	0.101	0.176	0.149	73.40	6.42
31	8	0.103(Run no 2 in Table 1)	0.102	0.193	0.159	77.56	4.79
32	10	0.102(Run no 2 in Table 1)	0.102	0.198	0.168	82.35	3.56
33	12	0.102(Run no 2 in Table 1)	0.102	0.194	0.166	81.37	3.16
34	4	0.101(Run no 6 in Table 1)	0.101	0.145	0.102	50.50	9.05
35	6	0.101(Run no 6 in Table 1)	0.101	0.153	0.113	55.94	7.24
36	8	0.101(Run no 6 in Table 1)	0.101	0.169	0.126	62.38	4.65
37	10	0.101(Run no 6 in Table 1)	0.101	0.164	0.120	59.41	5.13
38	12	0.101(Run no 6 in Table 1)	0.101	0.180	0.131	64.85	3.64

Table 4. Graft copolymers of RSS-3 with poly-MMA macroperoxy initiator at 90°C

Run No	Time (hour)	Poly-MMA initiator (g)	RSS-3 (g)	Yield (g)	Yield of Crosslinked Graft Polymer (g)		
					g	Con. (wt%)	q_v (in CH_3Cl)
39	4	0.101(Run no 2 in Table 1)	0.100	0.152	0.117	58.21	9.90
40	6	0.101(Run no 2 in Table 1)	0.102	0.165	0.120	59.11	8.41
41	8	0.101(Run no 2 in Table 1)	0.101	0.184	0.131	64.85	6.78
42	10	0.101(Run no 2 in Table 1)	0.101	0.182	0.128	63.37	4.32
43	12	0.101(Run no 2 in Table 1)	0.100	0.193	0.135	67.16	3.50
44	4	0.101(Run no 6 in Table 1)	0.101	0.148	0.098	48.51	11.12
45	6	0.101(Run no 6 in Table 1)	0.101	0.141	0.094	46.53	8.33
46	8	0.101(Run no 6 in Table 1)	0.100	0.158	0.109	54.23	5.19
47	10	0.101(Run no 6 in Table 1)	0.100	0.165	0.118	58.71	4.14
48	12	0.101(Run no 6 in Table 1)	0.101	0.173	0.127	62.87	4.55

**Fig. 1.** ¹H-NMR spectrum of poly-MMA macroperoxy initiator (run no 5 in Table 1).

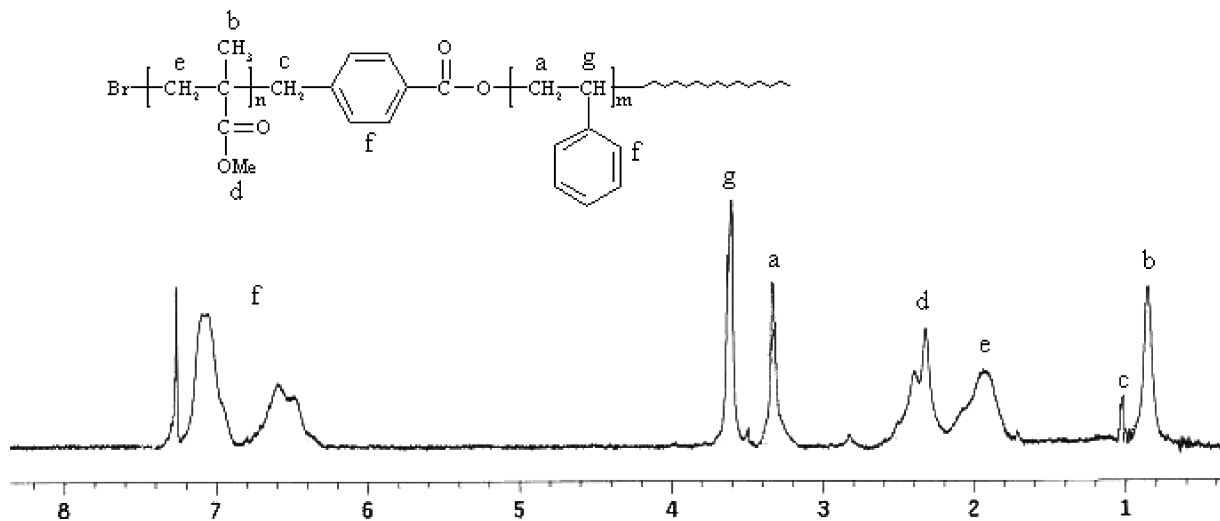


Fig. 2. ¹H-NMR spectrum of poly (MMA-b-S) block copolymer (run no 11 in Table 2).

benzoyl peroxide, 1.0. ppm for –CH₃ protons of MMA, 1.8 ppm for –CH₂ protons attached benzoyl group, 3.5 ppm for –OCH₃ protons of MMA, 3.6 ppm for –CH₂ protons of MMA, 7.4 and 7.8 ppm for aromatic ring protons of benzoyl group. The ¹H-NMR spectrum of poly (MMA-b-S) block copolymer (Fig. 2) shows 0.9 ppm for –CH₃ protons of MMA, 1.1 ppm for –CH₂ protons attached benzoyl group, 2.0 ppm –OCH₃ protons of MMA, 2.4 ppm for

–CH₂ protons of MMA, 3.3 ppm for –CH₂ protons of S, 3.7 ppm for –CH protons of S, 6.8 and 7.1.0 ppm for aromatic ring protons of S and the poly-MMA macroperoxy initiator. The FT-IR spectrum of poly (MMA-g-PBd) graft copolymer (Fig. 3) shows 755 cm⁻¹ for 1,4 di-substitution of benzoyl peroxide, 1179 and 1200 cm⁻¹ for –C–O groups of MMA and benzoyl peroxide, 1752 cm⁻¹ for –C–O groups of MMA and benzoyl peroxide, 2857, 2926 and 2961 cm⁻¹

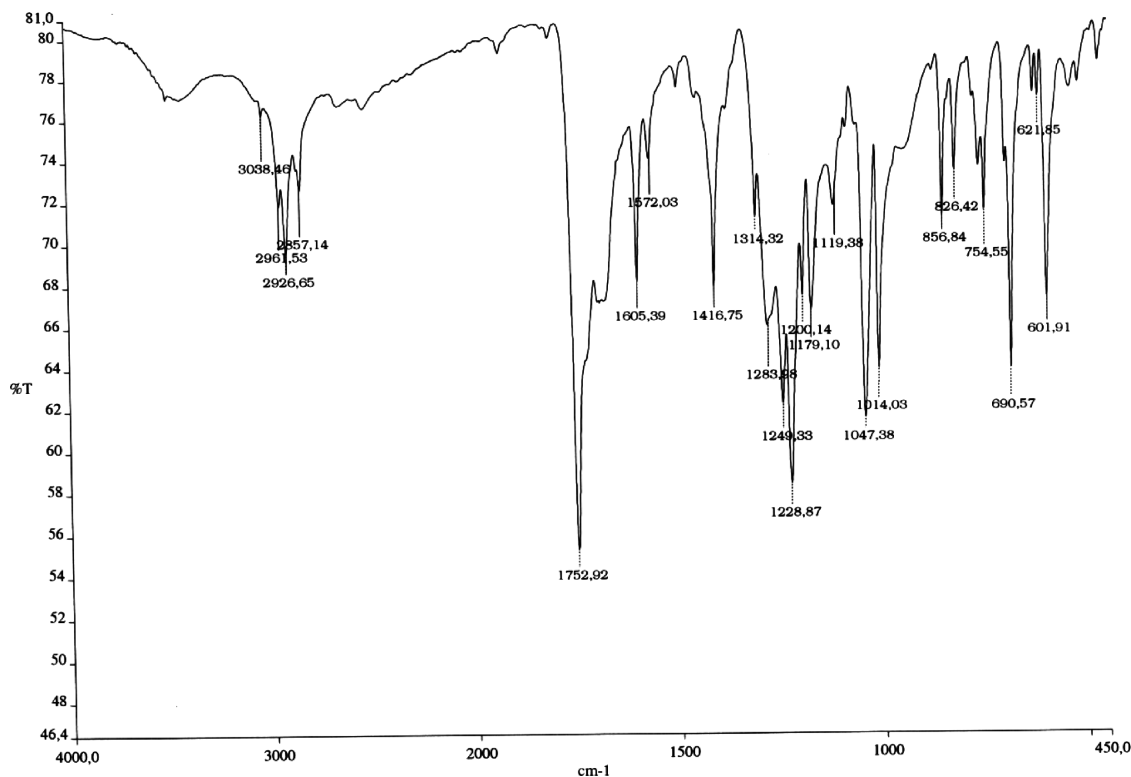


Fig. 3. FT-IR spectrum of crosslinked poly (MMA-g-PBd) graft copolymer (run no 31 in Table 3).

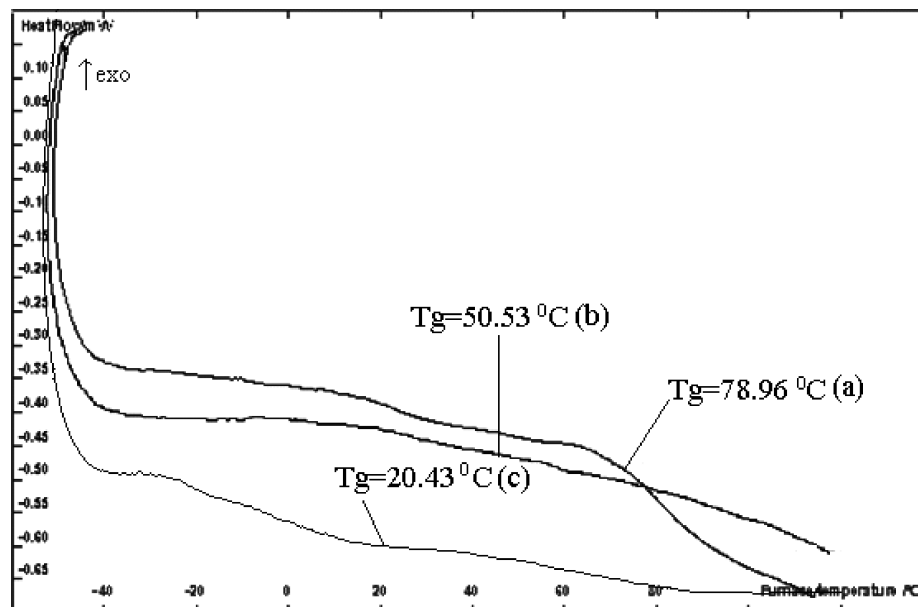


Fig. 4. DSC curves of the polymers (a) poly-MMA initiator (run no 5 in Table 1); (b) poly (S-b-MMA) block copolymer (run no 11 in Table 2); (c) poly (MMA-g-PBd) graft copolymer (run no 31 in Table 3).

for $-\text{CH}_2$ and $-\text{CH}$ groups of MMA, benzoyl peroxide and PBd, 3038 cm^{-1} for $-\text{CH}$ group of benzoyl peroxide.

Thermal analysis of the poly-MMA macroperoxy initiators, the block and graft copolymers were carried out by taking DSC curves. All samples exhibited glass transition

temperatures (T_g). The reported T_g values were obtained from the second heating curves. T_g value of the poly-MMA macroperoxy initiator was 78.96°C (run no 5 in Table 1) in Figure 4a. T_g value of poly (MMA-b-S) block copolymer was 50.53°C (run no 11 in Table 2) in Figure 4b. T_g values

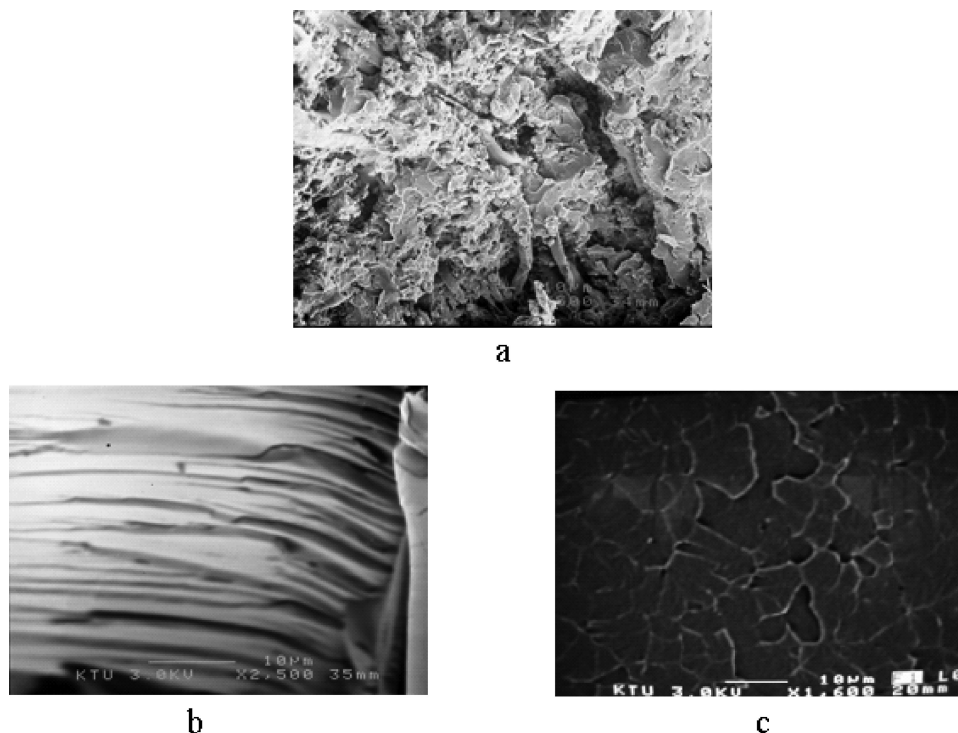


Fig. 5. SEM micrographs of the polymers (a) poly-MMA initiator ($\times 750$) (run no 6 in Table 1); (b) poly (S-b-MMA) block copolymer ($\times 2500$) (run no 11 in Table 2); (c) poly (MMA-g-PBd) graft copolymers ($\times 1600$) (run no 31 in Table 3).

Table 5. The strain-stress results of the polymer samples

Run No	Polymer Samples	Elastite Modulus (MPa)	Tensile Strengths (MPa)	Elongation (%)
49	Run no 5 in Table 1	2305.6	34.5	3.0
50	Run no 6 in Table 1	2611.4	37.0	4.0
51	Run no 7 in Table 1	2784.8	46.5	6.0
52	Run no 8 in Table 1	3176.4	45.5	5.0
53	Run no 12 in Table 2	2785.4	28.5	4.0
54	Run no 14 in Table 2	3146.4	29.0	3.0
55	Run no 17 in Table 2	3354.9	30.0	6.5
56	Run no 42 in Table 4	236.1	36.4	40.0
57	Run no 47 in Table 4	277.7	31.3	45.0

of poly (MMA-g-PBd) graft copolymer was 20.43°C (run no 31 in Table 3) in Figure 4c. T_g value reported in the literature for homo PMMA, for homo PS, for homo PBd as 105°C, 100°C, -102°C (39), respectively. T_g values of the block and graft copolymers changed to the value which was less than the value of poly-MMA initiator because of PS and PBd segments, respectively. The only one glass transition temperature value for the poly-MMA macroperoxy initiators, the block and graft copolymers show the miscible nature of the related polymers.

Block copolymers were purified by using the fractional precipitation technique, and no considerable amount of homopolymer was determined by the fractional precipitation. When the solvent was THF and the nonsolvent was petroleum ether, the gamma (γ) values of the block copolymers were between 1.38 and 1.88, while γ values for homo PMMA was 0.50–0.55 (33) and for homo PS was 2.5–3.2 (33). γ values of the block copolymers were between that of homo PMMA and that of homo PS. γ Values of the block copolymers were of higher value than that of homo PMMA because of PS segments. Fractional precipitation behavior provides evidence for the formation of block copolymer.

SEM micrographs of the polymers were taken for the surface morphology characterization of the polymers. The polymers were coated with a thin layer of gold on their surfaces to provide electrical conductivity. The micrographs were photographed from different views. Poly-MMA initiator exhibits a continuous phase as shown in Figure 5a. The SEM micrograph of poly(MMA-b-S) block copolymer shows a smooth surface (Figure 5b). According to the SEM micrographs of the block copolymer, homogenization of the block copolymer was good. Figure 5c shows the SEM micrographs of poly(MMA-g-PBd) graft copolymer. The rate of crosslinking increases with the increase of the crosslinker amount. Thus, smaller pore sizes are expected with increasing of the crosslinking. It can be seen from Figure 5c that the gel consists of a dense packing of rather large pores, separated by porous walls with channels.

The mechanical test specimens were punched from the well dried samples. Young's modulus (E-modulus), the strain at break and tensile strength values of the polymers

is shown in Table 5. The strain at break of the poly-MMA was changing in the range from 3 to 6%, while that of block copolymer was from 3 to 6.5%. E-modulus of the poly-MMA was changing in the range from 2305.6 MPa to 3176.4 MPa, while that of the block copolymer was from 2785.4 MPa to 3354.9 MPa. Tensile strength values of the poly-MMA were changing in the range from 34.5 MPa to 46.5 MPa, while that of the block copolymer was from 28.5 MPa to 30.0 MPa. E-modulus was 2400–3100 MPa for homo PMMA (40), 2800–3500 MPa for homo PS (41). Tensile strength values were 41–83 MPa for homo PMMA (40), 25–50 MPa for homo PS (42). The strain at break was 2–10% for homo PMMA (41), 2% for homo PS (42). E-modulus and the strain at break values of poly (MMA-b-S) block copolymers were between the values of their respective homopolymers. Tensile strengths of the block copolymers reported here were less than those reported in the literature for homo PMMA. E-modulus values calculated for the block copolymers were higher than that of homo PMMA reported in the literature. The elongation of the graft copolymer samples was in the 40–45% range. In general, graft copolymers have higher elongations when compared to that of the poly-MMA initiator because of excellent mechanical properties of PBd and RSS-3 segments. The elongation was 450–510% for homo PBd (40, 43). These results were more proof of the copolymer formation. Increase in elongation of the copolymer samples can be attributable to the plasticizer effect of the copolymer. It is obvious that E-modulus and the strain at break values of the polymers were proportional to the molecular weights, polymerization time and temperature.

4. Conclusions

A combination of ATRP and free radical polymerization was used in the synthesis of the block and crosslinked graft copolymers. Generally, ATRP are carried out at high temperatures. However, we have reported that ATRP is particularly effective in the bulk under low temperatures. ATRP can be used successfully to control the

polymerization of MMA over a broad range of molecular weights, reaching low polydispersities, with easy reaction conditions. The resulting poly-MMA macroperoxy initiators did not lose their peroxy groups after the ATRP at low temperatures. Poly(MMA-*b*-S) block copolymers and the crosslinked poly(MMA-*g*-PBd) and poly(MMA-*g*-RSS-3) graft copolymers could be prepared by using these macroperoxy initiators. For the polymers synthesized, a single glass transition temperature was determined showing miscible character. Graft copolymers have higher elongations when compared to that of the poly-MMA initiator because of excellent mechanical properties of PBd and RSS-3 segments.

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