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Synthesis of ABA triblock copolymers of *N*-substituted maleimides and methacrylates by group transfer polymerization

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Summary

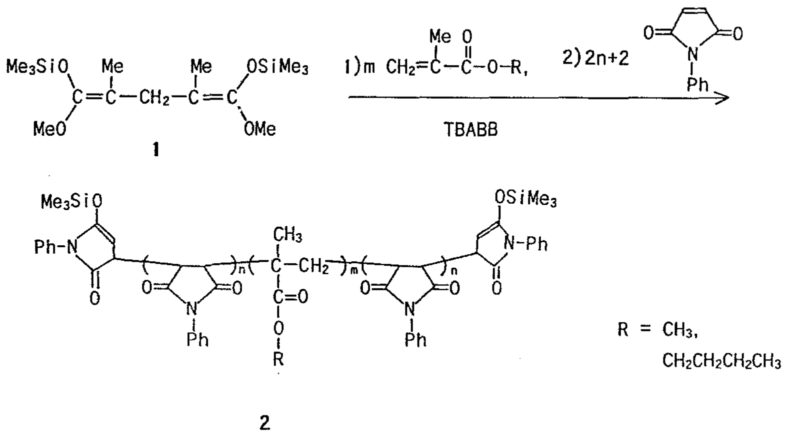
ABA type block copolymerization of N-phenylmaleimide (NPM), N-hexyl maleimide (NHM), methyl methacrylate (MMA), and butyl methacrylate (BMA) was investigated by group transfer polymerization (GTP) with [1,5-bis (trimethylsilyloxy)-1,5-dimethoxy-1,4-pentadiene] (**1**) as difunctional initiator. A novel block copolymers (**2**) of NPM and MMA (or BMA) could be prepared by sequential addition of NPM to the living PMMA (or PBMA) produced with **1**. The reaction did not exhibit the characteristics of living polymerization when NPM was added. The resulting copolymers showed good thermal stability. On the other hand, gelation occurred in GTP of NHM.

Introduction

Group transfer polymerization (GTP) has been a useful method for polymerization of vinyl monomers possessing one carbonyl group such as (meth)acrylates, N,N-dimethylacrylamide, and (meth)acrylonitrile with precisely controlled molecular weights and macromolecular architectures (1-4). It has also been reported GTP of vinylene monomers such as N-phenylmaleimides and the thermal properties of the resulting polymers (5). In our earlier report, many kinds of ABA block copolymers of (meth)acrylates were synthesized with difunctional initiators and characterized as architecturally well-defined polymers (6). The present study deals with the synthesis of **2** by GTP with the difunctional initiator and GTP behaviors and thermal properties of the resulting polymers.

Results and discussion

Copolymer samples **2** were prepared by sequential GTP of the monomers with the difunctional initiator at room temperature (Scheme 1). The block copolymers obtained by this method were yellow powders which were soluble in THF, DMSO, DMF, acetone, and insoluble in alcohol, ether, and hydrocarbon solvents. The results of the block copolymerization are summarized in Table 1. Almost quantitative



Scheme 1.

conversions were achieved in the case of poly(MMA) or poly(BMA), however, those were not consistent when NPM was added. Attempts at GTP of first addition of NPM followed by second addition of methacrylates resulted low conversions. The polydispersities of polymers were increased after NPM was added. These results indicate that chain transfer or termination reactions occur during GTP of NPM, and that living polymerization conditions have not been realized with addition

Table 1
ABA block copolymerization of NPM by GTP[a, b]

Exp.	monomer[c]	initiator	$\bar{M}_n \times 10^{-3}$		$\bar{M}_w/\bar{M}_n$	NPM content[e]
No.	(mmol)	(mmol)	theor[d].	obsd.		(mol %)
1	1. BMA(12.75) 2. NPM(14.6)	0.362	12.0(5.0)	16.6(4.9)	3.47(1.10)	52
2	1. NPM(10.5) 2. BMA(25.5)	0.362	15.0(5.0)	9.8(8.1)	3.73(3.18)	83
3	1. BMA(25.5) 2. NPM(12.75)	0.362	16.0(10.0)	24.3(7.9)	4.05(1.48)	29
4	1. MMA(25.5) 2. NPM(12.75)	0.724	6.5(3.5)	13.2(3.6)	2.40(1.16)	30
5	1. NPM(12.75) 2. MMA(25.5)	0.362	13.1(6.1)	10.2	6.18	81

a) Catalyst ; TBABB (0.1 M in THF), solvent ; THF
b) The values in parenthesis indicate the $\bar{M}_n$'s or polydispersities of the starting polymers.
c) (1) B block ; (2) A block in ABA triblock copolymer.
d) $\bar{M}_n$ values of theor. were calculated by the ratios of the monomers to the initiator.
e) Calculated from elemental analysis.

of NPM.

Figure 1 shows a typical ^{1}H NMR spectrum of poly(NPM-b-BMA-b-NPM) prepared by GTP. The signals assigned to the phenyl and methine protons of poly(NPM) block are observed at 7.2 ppm and from 3.0 to 4.0 ppm. The peaks assigned to the methyl and methylene protons of poly(BMA) block are observed from 0.8 to 4.0 ppm. Figure 2 shows typical GPC curves of the polymers. The peak of starting poly(BMA) shifts toward the higher molecular weight copolymer of wider molecular weight distribution. These results suggest that poly(NPM-b-BMA-b-NPM) can be obtained by adding NPM to living poly(BMA), but it is polydisperse in size and composition.

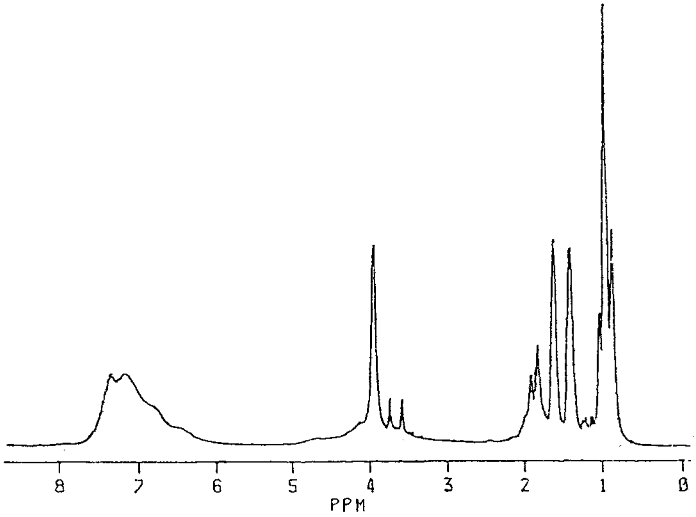


Figure 1. ^{1}H-NMR spectrum of poly(NPM-b-BMA-b-NPM) (Exp. No.1)

In the case of poly(BMA-b-NPM-b-BMA) (Exp. No.2), the molecular weight of resulting polymer did not increase appreciably after addition of second monomer, BMA, and the NPM content of the copolymer was much higher than predicted. The polymer consisted of homopolymers and structurely nonuniform block copolymers. These results are correspondent to the fact that NPM is more reactive than BMA and MMA in GTP(5).

Therefore, a ABA block copolymer composed of middle block of poly(methacrylates) and outer block of poly(NPM) can be prepared by difunctional initiator **1**.

The copolymers show good thermal stability in comparison with PMMA and PBMA. As shown in Figure 3, poly(NPM-b-MMA-b-NPM) undergoes no substantial weight loss below 400℃. The half weight loss temperature (T_{50}) is about 430℃ and the residual weight at 500℃ about 10 %.

When TBABB was added to a solution of NHM with or without initiator **1**, the solution turned to orange color and gelation occurred with mild exotherm. A small particles identified to contain 32 mol % of NHM by elemental analysis were precipitated by sequential addition of NHM

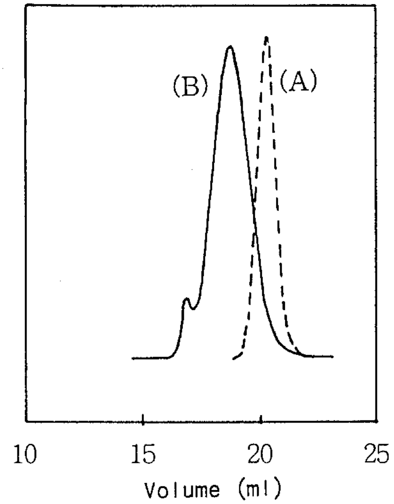


Figure 2. GPC charts of (A) starting poly(BMA) and (B) block copolymer (Exp. No.1)

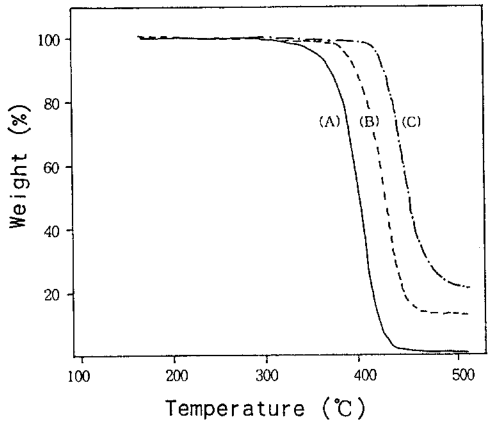


Figure 3. Thermogravimetric analysis of (A) PMMA (B) poly(NPM-b-MMA-b-NPM) (Exp. No.4) and (C) PNPM

to the living poly(MMA) in THF. The soluble part in DMSO was found to be almost PMMA from ^{1}H-NMR analysis. From the above results, it is assumed that side reactions such as carbonyl addition or ring opening of imide group of NHM take place predominantly in the presence of TBABB (7).

Experimental

Materials

Tetrahydrofuran (THF) was distilled from sodium and benzophenone immediately prior to use. BMA and MMA were purified by stirring over finely ground calcium hydride followed by distillation under reduced pressure. N-Phenylmaleimide (NPM) was commercially available and used after several recrystallizations. Difunctional initiator **1** was prepared according to a previously published procedure (6). The synthesis of Tetrabutylammonium bibenzoate (TBABB) was described elsewhere. (8)

Preparation of N-hexylmaleimide (NHM)

In a 500 ml three-neck flask provided with a stirrer, a reflux condenser and a dropping funnel were placed 19.6 g (0.2 mol) of maleic anhydride and 250 ml of ethyl ether at 0℃. Freshly distilled hexyl amine (20.24 g, 0.2 mol) was added dropwise over 30 min. to the flask. The reaction mixture was stirred overnight. The white powder was collected by filtration and added to a mixture of 100 ml of acetic anhydride and 10 g of anhydrous sodium acetate. The resulting mixture was heated with stirring until the internal temperature reached 90 -

95℃. Heating and stirring were maintained for one hour. After cooling, the reaction mixture was poured into a large amount of ice water and was neutralized with sodium carbonate. The organic layer was extracted with ethyl acetate followed by concentration. The product was distilled in vacuo to yield 15 g (41 %) of colorless liquid, b.p., 90℃/0.1 torr; ^{1}H-NMR ($CDCl_3$) δ 0.81 (t, 3H), 1.21 (m, 2H), 1.51 (m, 2H), 3.44 (t, 2H), 6.63 (s, 2H) ; ^{13}C-NMR ($CDCl_3$) δ 13.87 (CH_3-), 22.38, 26.28, 28.38, 31.18 (-$(CH_2)_4$-), 37.81 (N-CH_2-), 133.94 (-CH=), 170.79 (C=O)

Polymerization procedure

For example, a 100 ml three neck flask fitted with an argon inlet, a magnetic stirrer, and a thermocouple was charged with THF (17 ml, via cannular), TBABB (0.144 ml), and a difunctional initiator **1** (0.2 ml, 0.362 mmol). Then BMA (1.81 ml, 25.5 mmol) was added dropwise via syringe. After stirring for an hour a 10 ml aliquot (12.75 mmol of BMA) of the reaction mixture was withdrawn for analysis. From the aliquot, by evaporation of THF, homopoly(BMA) was obtained ; $\overline{M}_n$ = 4900, $\overline{M}_w/\overline{M}_n$ = 1.10. To the reaction mixture, additional TBABB (0.36 ml) and 14.6 mmol of NPM (9.7 ml, 1.5 M in THF) was added sequentially. After stirring additional an hour 5 ml of methanol was added and the reaction mixture was poured into an hexane-ether-methanol (volume ratio 5:3:2) mixture. The precipitate was collected by filtration, washed with ether and methanol, and dried in vacuo ; $\overline{M}_n$ = 16600, $\overline{M}_w/\overline{M}_n$ = 3.47 Anal. Found : C, 66.8 % ; H, 6.5 % ; N, 4.5 %.

Measurements

^{1}H-NMR spectra were recorded at Brucker AC-200. Elemental analysis were performed with Heraeus Elemental Analyzer. Gel permeation chromatography (GPC) was measured on a Waters 150C with refractive index detector with ultrastyragel columns with THF eluent. PMMA standards were used for the construction of a calibration curve. Thermogravimetric analyses were carried out on a TGA V2. OB Dupont 9900 in a nitrogen stream at a heating rate 20℃ per minute.

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References

1. O. W. Webster, W. R. Hertler, D. Y. Sogah, W. B. Farnham, and T. V. Rajanbabu (1984) J. Am. Chem. Soc. 105 : 5706
2. W. B. Fahnham and D. Y. Sogah (1986) Polym. Prep. 27 : 167
3. O. W. Webster (1990) Makromol. Chem., Macromol. Symp. 33 : 133
4. W. J. Brittain and I. B. Dicker (1989) Macromolecules 22 : 1054
5. A. Saito and D. A. Tirrell (1994) Polym. J. 26 : 169
6. (a) H. S. Yu, W. J. Choi, K. T. Lim and S. K. Choi (1988) Macromolecules 21 : 2893 ; (b) W. J. Choi, Y. B. Kim, K. T. Lim, and S. K. Choi (1990) Macromolecules 23 : 5365 ; (c) W. J. Choi, K. T. Lim, S. K. Kwon, and S. K. Choi (1993) Polym. Bull. 30 : 401
7. (a) R. C. P. Cubbon (1965) Polymer 6 : 419 ; (b) T. Hagiwara, T. Someno, H. Hamana, and T. Narita (1988) J. Polym. Sci. Polym. Chem.

Ed. 26 : 1011 ; (c) T. Hagiwara, T. Shimizu, T. Someno, T. Yamagishi, H. Hamana, and T. Narita (1988) Macromolecules 21 : 3324

8. I. B. Dicker, G. M. Cohen, W. B. Fahnham, W. R. Hertler, E. D. Laganis, and D. Y. Sogah (1990) Macromolecules 23 : 4034