NOTES

Block Copolymerization of Methacrylates Using Ph₂PCl/Epoxide as Preinitiator

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Developing block copolymerizations with usually available initiator system is strongly required in industrial process.[1] Recently, living-like radical polymerization systems depending on the initiators such as nitrooxide compounds 2,2,6,6-tetramethyl-1-piperidinyloxy, free radical (TEMPO) or Cu(I)/bipyridine provided useful methods to prepare polystyrenic[2] block copolymers and polymethacrylic[3] block copolymers, respectively. Group transfer polymerization is also attractive to prepare blocked polymethacrylic copolymers.[4] These initiator systems make the block copolymerizations running at a relatively simple experimental condition. However, inducing living ability of the propagating end with currently available reagent (lower cost) and easier demand is still important in the synthetic polymer chemistry. In our recent work, it was found that the chlorodiphenylphosphine (CDP) can initiate the polymerization of methacrylates in the presence of epoxy compounds.[5,6] Particularly, this method gives high molecular weight polymers with general synthetic operation.[6] We propose that the polymerization proceeds by way of group-transfer mechanism with forming phosphino enolate site that has long lifetime to give favorably high molecular weight polymer. In this paper, we report that the initiator of CDP/epoxide is utilizable in the block copolymerization of methacrylates.

EXPERIMENTAL

The monomers, methyl methacrylate (MMA), *n*-butyl methacrylate (*n*-BMA), *t*-butyl acrylate (*t*-BA), benzyl methacrylate (BzMA), cyclohexyl methacrylate (c-HMA), *n*-butyl methacrylate (*n*-BMA), methyl acrylate (MA), tetrahydrofurfuryl methacrylate (TFMA), cyclohexyl acrylate (c-HA), and glycidyl methacrylate (GMA) were purchased from Tokyo Kasei Inc. and used after passing through a silica column and drying on 4 Å molecular sieves. GMA was used as epoxide fraction in preinitiator. CDP was purchased form Tokyo Kasei Inc. and used as obtained. *N,N*-Dimethylformamide (DMF) (anhydrous degree) was obtained from Wako

Chemcal Co.

### Synthesis of Poly(BzMA-b-TFMA)

A 50 ml, one necked round bottomed flask, fitted with magnetic stirring bar, and three-way cock, was flushed with argon under reduced pressure and heated condition. With flushing by argon, DMF (10 ml), TFMA (2.37 ml, 14.5 mmol), CDP (0.09 mmol, 0.1 ml from 0.2 g ml⁻¹ toluene solution), and then GMA (0.01 ml) were added to the flask with syringes, respectively. The mixture was stirred for 24 h at 60°C. After adding again 5 ml of DMF, a small amount of solution was taken by syringe from the reaction mixture for GPC (molecular weight) and ¹H NMR (conversion) measurements. The second monomer, BzMA (2.46 ml, 14.5 mmol), was added by syringe and the mixture was stirred for further 24 h at the same temperature. After taking a small amount of the solution for measurement of GPC and ¹H NMR, 20 ml of chloroform was added. The solution was poured into a large amount of methanol. The precipitates were washed by methanol and dried. Yield 75% (based on the total amount of TFMA and BzMA) with M_n 89 × 10³ and 2.94 polydispersity.

The other block copolymers were prepared through the same procedure with identifying the conversion of M_1.

Characterizations of the Polymers

Conversion of the monomers M_1 and M_2 was evaluated by ¹H NMR (250 MHz, Bruker AC 250P, in CDCl₃ relative to tetramethylsilane (TMS) standard at $\delta = 0$) with comparing the integration values for COOCH₂ residues on side chain of polymer and on the unreacted monomer. The composition (in mol%) for the blocked copolymers was also estimated by ¹H NMR from the integration ratio for M_1 and M_2 residues. GPC measurement was made by the Analytical Dept. Dainippon Ink & Chemicals Inc. (HLC-08 GPC system equipped with Showa Denkou columns, tetrahydrofuran (THF) as eluent).

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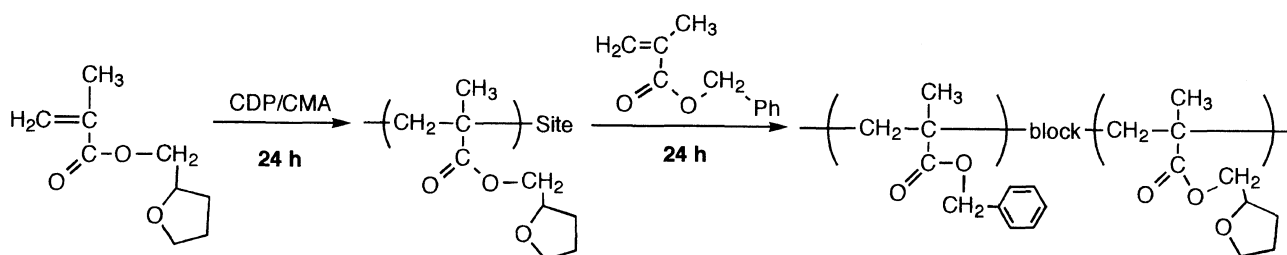
Scheme 1.

Table I. Monomer structures and yields of polymethacrylates[a]

Monomer	Yield/%
n-BMA	93
n-BA	92
c-HA	91
TFMA	90
MMA	80
MA	54

[a] [Monomer]/[CDP] = 160/1; CDP, 9.06×10^{-2} mmol; GMA, 0.01 ml; DMF, 5.0 ml; 24 h, 60°C under Ar.
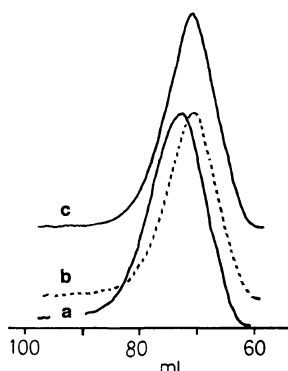

Figure 1. GPC profiles for polymers in block copolymerization: (a) The first stage polymer, poly(TFMA), obtained after 24 h; (b) second stage polymer, poly(BzMA-b-TFMA), obtained after 24 h from adding BzMA; (c) final sample, poly(BzMA-b-TFMA), after precipitated.

Figure 2. ^1H NMR profiles for polymers: (a) poly(BzMA); (b) poly(BzMA-b-TFMA); (c) poly(BzMA-co-TFMA).

RESULTS AND DISCUSSION

To use CDP/epoxide as initiator in block copolymerization, whether the first monomer is highly consumed in a selected condition should be confirmed. We investigated first the relations between the structure of monomers and yield of polymers in DMF solvent. Table I shows the results. Within 24 h reaction time at 60°C, the monomers such as n-BMA, n-BA, c-HA, and TFMA, are well polymerized and the yields of the corresponding polymers were over 90%. Hence, it seems that those monomers, i.e., methacrylates and acrylates, can be used as M_1 monomers in block copolymerization.

Ushing TFMA and BzMA as M_1 and M_2, respectively, block copolymerization was examined as shown in Scheme 1 and Figure 1. It was found that the conversion of TFMA by 24 h was 92% and the corresponding polymer showed 47×10^3 number averaged molecular weight (M_n) with 3.45 polydispersity. After second monomer, BzMA, was added into the polymer solution and stirred further for 24 h, the conversion of BzMA was found to be 72% and the M_n increased to 79×10^3 with
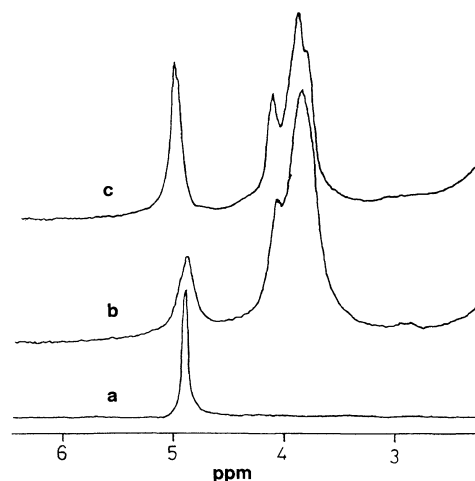
3.28 polydispersity. This indicates that the block copolymerization may proceed smoothly. After reprecipitation and drying, the block copolymer having 89×10^3 M_n with 2.94 polydispersity, was obtained in 75% yield. The mole ratio of M_1 to M_2 in this copolymer was determined 48/52 by ^1H NMR spectroscopy. Figure 2 showed the ^1H NMR profiles for block and random copolymers obtained from BzMA/TFMA and for poly(BzMA) with (CDP/GMA) initiator, respectively. The random copolymer (composition ratio TFMA/BzMA = 50/50) showed methylene signal of benzyl residues at 4.96 ppm. In comparison with the random copolymer, the methylene peak for the block copolymer resonated at 4.87 ppm, as in the case of homopolymer poly(BzMA). The 0.1 ppm up-field shift for the block copolymer may be due to the ring-current effect of benzene ring[7] where the side benzyl groups on BzMA block are neighboring each other as like with poly(BzMA). In random copolymer, monomers M_1 and M_2 may be highly alternative in the main chain. This would reduce the ring current effect between benzyl groups on side chains. The block copolymerization of TFMA with BzMA was influenced by the solvent amount (see Table II). After M_1 polymerized for 24 h in definite amount of DMF (10 ml), further addition of DMF in block copolymerization stage rose up the conversion of M_2 and yields of the copolymer. The composition of M_2 in the block copolymer also increased progressively with addition of DMF after M_1 polymerized.

Selecting n-BMA as M_1 monomer, block copolymerization was carried out using MMA, BzMA, MA, c-HA, and TFMA as M_2 monomers according to the above method for 24 h and further 24 h. As summarized in Table

Table II. Block copolymer obtained from TFMA (M_1) and BzMA $(M_2)^a$

DMF in ml	Conversion/%	Yield	Composition[b]	$M_n \times 10^{-3}$	M_w/M_n
1st stage/2nd stage	M_1/M_2	%	M_1/M_2		
10/0	90/42	56	61/39	80	2.76
10/5.0	92/72	75	48/52	89	2.94
10/10	89/95	85	39/61	59	3.17

[a] CDP, 9.06×10^{-2} mmol; $[M_1]/[M_2]/[CDP] = 160/160/1$; GMA, 0.01 ml; 60°C, 24 h/24 h, Ar.   [b] In mole ratio.

Table III. Block copolymerization of n-BMA (M_1) with various monomers $(M_2)^a$

M_2	Conversion/%	Yield	Composition[b]	$M_n \times 10^{-3}$	M_w/M_n
	M_1/M_2	%	M_1/M_2		
MMA	100/88	96	53/47	25	2.27
BzMA	77/83	83	64/34	64	3.28
MA	88/86	58	47/53	71	3.19
c-HA	90/95	98	50/50	39	3.24
TFMA	—	63	—	97	2.58

[a] CDP, 9.06×10^{-2} mmol; $[M_1]/[M_2]/[CDP] = 160/160/1$; GMA, 0.01 ml; 60°C, 24 h/24 h, Ar.   [b] In mole ratio.

Table IV. Block copolymerization of c-HA (M_1) with various monomers $(M_2)^a$

M_2	Conversion/%	Yield	Composition[b]	$M_n \times 10^{-3}$	M_w/M_n
	M_1/M_2	%	M_1/M_2		
MA	100/49	77	71/29	41	2.43
n-BA	96/60	81	77/23	44	2.24
MMA	94/71	84	63/37	39	2.11
n-BMA	100/35	61	82/18	32	3.95
BzMA	96/49	79	80/20	69	3.40

[a] CDP, 9.06×10^{-2} mmol; $[M_1]/[M_2]/[CDP] = 160/160/1$; GMA, 0.01 ml; 60°C, 24 h/24 h, Ar.   [b] In mole ratio.

III, poly(n-BMA) obtained from first stage blocks not only with methacrylates but also with acrylates to give the corresponding block copolymers. The compositions of M_1 to M_2 on the copolymers are nearly half and half except for the case of BzMA.

By the same method, c-HA was used as M_1 monomer to prepare block copolymers in which acrylates and methacrylates were used as M_2 monomers (Table IV). The conversion of M_1 (c-HA) within 24 h was very high. However, the conversion of M_2 after 24 h was in the range 35—70%, depending on the structure of the monomers. M_2 content in the block copolymers (calculated from ^{1}H NMR using the reprecipitated samples) is below 40 mol% due to lowering M_2 conversion. Compared to the poly(n-BMA), the polymeric chain of poly(c-HA) is very soft. This feature may affect the propagating ability of the second block leading to decrease of the conversion of M_2 monomers. Selecting of the M_1 monomers for block copolymerization in the CDP/epoxide initiator system should thus be based not only on the polymerizability of M_1 but also on the property of the polymer formed from M_1.

All block copolymers discussed above showed unimodal GPC trace although the values of the molecular distribution varied between 2 and 3.5. The broad distribution would be determined by the case of the first stage polymerization. CDP/epoxide preinitiator system cannot control molecular weight in solvent polymerization because the true phosphorous initiator is generated

from the reaction between CDP and monomer in the presence of epoxide. Without epoxide participation, no polymerization of the monomers can occur at 60°C even for a long reaction time. We should show that the consumption of the M_1 monomers in the first stage is high, but not complete. Thus, the remaining M_1 monomer must be introduced randomly to the second block in the stage of block copolymerization.

In conclusion, the CDP/epoxide preinitiator system can be used for block copolymerization of methacrylates with a convenient procedure.

REFERENCES

1. R. P. Quirk and J. Kim, Rubber Chem. Technol., **64**, 450 (1991); O. W. Webster, Science, **251**, 887 (1991).
2. M. K. Georges, R. P. N. Veregin, G. K. Hamer, and M. P. Kazmaier, Macromol. Symp., **88**, 89 (1994); E. Yoshida, T. Ishizone, A. Hirao, S. Nakahama, T. Takata, and T. Endo, Macromolecules, **27**, 3119 (1997); T. Fukuda, T. Terauchi, A. Goto, Y. Tsujii, and T. Miyamoto, Macromolecules, **29**, 3050 (1996).
3. T. P. Patten, J. Xia, T. Abernathy, and K. Matyjaszewski, Science, **272**, 866 (1996) and cited therein.
4. D. Y. Sogah, W. R. Hertler, O. W. Webster, and G. M. Cohen, Macromolecules, **20**, 1473 (1987).
5. R.-H. Jin and T. Nishikubo, Polymer, **35**, 2907 (1994).
6. R.-H. Jin, Y. Hanazaki, and T. Nishikubo, Polym. J., **29**, 113 (1997).
7. F. A. Bovey, "High Resolution NMR of Macromolecules," Academic Press, New York & London, 1976, Chapter X.