SHORT COMMUNICATIONS

On the Copolymerization Reactivity of Macromonomers

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In the past few years, the number of studies on the synthesis and copolymerization of macromonomer has rapidly increased because of the recognition of its useful and important synthetic routes of well-defined graft copolymers by which the number and length of branch segments can be controlled.^{1–8} However, the copolymerization behavior of the macromonomer is not well understood at present.^{9–14} On the reactivity of macromonomer, the following can be considered as the major factors influencing on it: i) copolymerization reactivity of the polymerizable end group associated with the chemical structure of the end group,^{15,16} ii) kinetic excluded volume effect related to the diffusion control reaction process due to the large size of macromonomer and the topological resistance against the diffusion of the reactive end group,^{17,18} and iii) non-homogeneous distribution of the polymerizable end group in the reaction system due to the thermodynamic repulsive interaction between a macromonomer and a propagating comonomer chain associated with the incompatibility between unlike polymers.^{12,19–23}

In this paper, we studied the copolymerization behavior of a macromonomer to examine the effect of the thermodynamic repulsive interaction on the copolymerization reac-

tivity of macromonomer, and discuss the results in terms of the interpenetration of macromonomer coils and unlike propagating comonomer chains in the homogeneous solution.

The radical copolymerization of Styrene (St) macromonomer having a methacryloxy end group ($\bar{M}_n=12400$, $\bar{M}_w/\bar{M}_n=1.06$, end functionality=0.86)

with methyl methacrylate (MMA) (copolymerization system I), St (system II), and a mixture of them (system III) were carried out in benzene (total monomer:benzene=1:3 by weight) at 60°C with 0.6 mol% of AIBN as an initiator under vacuum in sealed glass ampules. In the copolymerization system I, St macromonomer was copolymerized with MMA comonomer to examine the effect of the thermodynamic repulsive interaction between the macromonomer and the unlike propagating comonomer chain on the copolymerization, where PSt-PMMA-benzene system is one of the typical polymer-polymer-solvent ternary systems. In the system II, St macromonomer was copolymerized with St comono-

Table I. Copolymerization of macromonomer^a

(I) Comonomer, MMA					(II) Comonomer, St					(III) Comonomer, St + MMA ^b				
Reaction time	Total conversion	M_n in copolymerization	Number of branch	$\bar{M}_n$ ($\times 10^{-3}$)	Reaction time	Total conversion	M_n in copolymerization	Number of branch	$\bar{M}_n$ ($\times 10^{-3}$)	Reaction time	Total conversion	M_n in copolymerization	Number of branch	$\bar{M}_n$ ($\times 10^{-3}$)
h	mol%	wt%			h	mol%	wt%			h	mol%	wt%		
1	8.6	53.3	1.8	41.2	1	0.4	—	—	—	1	15.3	59.5	1.4	28.9
3	22.9	52.4	1.9	45.2	3	2.6	92.4	2.4	31.6	2	21.0	44.4	1.4	40.1
5	37.1	49.0	2.0	50.4	8	12.2	81.6	2.6	37.8	4	24.3	50.5	1.5	36.5
8	42.5	51.2	2.3	54.7	13	27.4	67.2	2.1	39.0	6	29.4	46.3	1.1	28.2
13	70.2	46.5	1.6	42.0	18	28.3	66.6	2.2	41.1	9	31.4	50.7	1.5	36.9
20	76.2	50.6	1.9	47.3	24	36.3	62.3	2.2	43.9	12	40.0	39.4	1.3	40.1
30	84.4	46.8	1.8	46.9	48	46.4	59.9	2.1	43.6	24	54.1	46.5	1.5	40.0
48	96.4	50.4	1.9	46.4	86	73.5	51.7	1.5	36.7	48	76.6	43.9	1.5	43.6

^a Initial feed ratio: [Macromonomer]/[Comonomer] = 8.0×10^{-3} ; Macromonomer/Comonomer = 1.0 by weight; polymerization solvent, benzene; $V_s = 0.75$.^b St/MMA = 1.0 by weight.

mer where there is no thermodynamic repulsive interaction between unlike polymers. In the system III, the degree of the effect is expected to be between system I and II with respect to the average composition of the propagating comonomer chains.

Copolymerizations were carried out simultaneously in eight or nine ampules of the same condition to obtain both the time-conversion curves of a macromonomer and a comonomer, from which the instantaneous feed composition and the instantaneous copolymer composition were obtained. Conversion of a macromonomer and a comonomer were measured by Gel Permeation Chromatography (GPC) and Gas Chromatography (GC) with a internal standard (*n*-octadecane).

Copolymerization behavior of monomer-1 (M_1) and monomer-2 (M_2) is usually discussed on the basis of the well-known copolymerization equation,

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1](r_1[M_1] + [M_2])}{[M_2](r_2[M_2] + [M_1])}$$

where $[M_1]$ and $[M_2]$ are the molar concentrations of M_1 and M_2 , and r_1 and r_2 are the respective monomer reactivity ratios. When M_1 is comonomer and M_2 is macromonomer, the relative copolymerization reactivity of macromonomer is evaluated by $1/r_1$, i.e., the ratio of rate constant for a propagating comonomer radical adding macromonomer to the rate constant for its own comonomer, because the feed composition of macromonomer by mole is extremely low even at the high feed composition by weight in an ordinary system, which makes it difficult to determine the r_2 value. In this study, the $1/r_1$ values were determined by the following three methods to avoid error brought about with the approximation in each method by comparison of the results. (A): one parameter method of integral form,¹⁰ (B): Skeist's method in which experimental time-conversion curves were fitted to calculated instantaneous feed composition-degree of conversion

curves of different r_1 and r_2 to calculate $1/r_1$,^{11,24} (C): Fineman-Ross plot using the copolymerization data of low conversion with several feed compositions.^{12,24}

Table I summarizes the typical time-conversion data for the copolymerizations of the macromonomer in the three systems, in which the initial feed compositions of St macromonomer and comonomer were 0.5 by weight in all cases. Table II summarizes $1/r_1$ values obtained by the three methods described above together with the values of the copolymerization of corresponding small monomers.

It is seen in Table I that the macromonomer compositions in the produced graft copolymer in systems I and III are almost the same to the initial feed composition irrespective of the reaction time. On the other hand, the macromonomer composition in the graft copolymer is considerably higher than the initial feed composition in system II especially at the low conversion region. These can be reasonably explained in terms of monomer reactivity ratios of the polymerizable end groups of macromonomers and comonomers alone. That is, in system I, St macromonomer having a methacryloxy end group was copolymerized with

Table II. Macromonomer reactivity^a

System No.	Comonomer	$1/r_1$			$\bar{M}_n^b$ ($\times 10^{-3}$)
		(A)	(B)	(C)	
I	MMA	0.95	1.04	0.79	46.4
II	St	2.12	2.03	—	43.6
III	MMA/St	0.90	0.94	1.11	43.6

^a (A), one parameter method of integral form; (B), Skeist's equation; (C), Fineman-Ross plots of copolymerization equation.

$1/r_1$ values of the corresponding small monomers

i) copolymerization of M_1 (MMA) with M_2 : M_2 = MMA, 1.00; BMA, 1.27; DdMA, 0.82; BzMA, 1.17.

ii) copolymerization of M_1 (St) with M_2 : M_2 = MMA, 1.92; BMA, 1.85; DdMA, 1.76; BzMA, 2.17.

^b Number-average molecular weight of the graft copolymer after 48 hours copolymerization.

MMA comonomer, in which if the reactivity of the end group of macromonomer is predominant factor in determining the copolymerization, macromonomers can be expected to be copolymerized in an ideally random manner ($r_1=r_2=1.0$). In system II, on the other hand, the macromonomer was copolymerized with St comonomer in which the copolymerization is expected to be essentially equal to the copolymerization of St and MMA under the condition of the predominant effect of the polymerizable end group ($r_1=0.52$, $r_2=0.47$, $r_1r_2=0.244<1.0$). This means increased tendency of alternating copolymerization, resulting in higher reactivity of macromonomers than the ideal random copolymerization system. In system III, there are two kinds of comonomers, MMA and St, so that the alternating tendency of the methacryloxy group to St comonomer is smeared by the large amount of coexisting MMA comonomer resulting in giving the almost the same behavior to system I.

The predominant effect of the end group of macromonomer can also be seen in the values of $1/r_1$ in Table II. In this table, the $1/r_1$ values in each system are almost the same as the average values of the corresponding small monomers obtained in bulk and benzene solution copolymerization at 50–60°C (there is no particular solvent effect on r_1 and r_2 values in benzene),¹⁶ The $1/r_1$ value in the copolymerization of St (M_1) with MMA (M_2) is 1.92, with butylmethacrylate (BMA) is 1.82, with dodecylmethacrylate (DdMA) is 1.76, and with benzylmethacrylate (BzMA) is 2.22. Further, the value in the copolymerization of MMA (M_1) with BMA (M_2) is 1.27, with DdMA is 0.82, and with BzMA is 1.17. Schulz and Milkovich also reported the copolymerization of St macromonomer having a methacryloxy end group with MMA, St, ethyl and methyl acrylate in benzene–dimethylsulfoxide mixed solvent.¹¹ They obtained a $1/r_1$ value of 1.65 with St and nearly equal to 1.0 with MMA suggesting the large effect of the end group of the macromonomer on the copolymer-

Figure 1. Schematic representation of interpenetration of a macromonomer coil and a propagating comonomer chain. Partial polymer segments having a degree of polymerization less than $1/\chi_{\text{St-MMA}}(1-\phi_s)$ are compatible to each other in homogeneous solution copolymerization.

ization, which is consistent with our results.

These results mean that the copolymerization behavior of macromonomers is not affected or quite little affected by both their size (in a sense of the kinetic excluded volume effect) and thermodynamic repulsion between unlike polymer segments in this system. In another words, the results indicate that the two unlike polymer coils of a macromonomer and a propagating comonomer chain should extensively interpenetrate within the time scale of this homogeneous solution copolymerization as schematically shown in Figure 1, although they are incompatible at higher concentration or in bulk.

In the polymer–polymer–solvent ternary system, the effective Flory–Huggins interaction parameter between polymer-A and polymer-B is given by $\chi_{AB}^{\text{eff}} = \chi_{AB}(1-\phi_s)$ in the symmetrical system ($\chi_{AS} = \chi_{BS}$), where ϕ_s is the volume fraction of solvent. Further, a partial segment of each polymer having a degree of polymerization $N_p < 1/\chi_{AB}$ can be compatible even when the whole of the polymer chains are incompatible to each other.²³ In the PS–PMMA–benzene system, $\chi_{\text{St-MMA}}$ is estimated 0.036 using $\delta_A=9.0$ for PS, $\delta_B=9.5$ for PMMA¹⁶ at 60°C. Then χ_{AB}^{eff} is roughly estimated as 0.0090 or $(\chi_{AB}^{\text{eff}})^{-1} = 110$ at $\phi_s=0.75$, (initial total monomer concentration is 0.333 g/ml), indicating that partial segments of PS

and PMMA having a degree of polymerization less than 110 can be compatible to each other in a benzene solution at this concentration. This means that almost entire part of a macromonomer ($N_p = 124$) can penetrate into the coil of the propagating comonomer chain to be copolymerized. This feature may be related to the finding that no intramolecular phase separation of PSt-PMMA block copolymers was detected in dilute solution of mutual good solvents for both components, reported by Kotaka *et al.*²² However, there are several reports on the effect of the thermodynamic repulsive interaction between a macromonomer and a comonomer in other copolymerization system,¹²⁻¹⁴ which is presumably related to the volume fraction and the asymmetric nature of the copolymerization solvent for both components. This makes large difference in expansion or swelling of polymer coils in the solvent to change the degree of the interpenetration (in extreme case the solvent is preferential for one component and the copolymerization system becomes heterogeneous resulting in the interpenetration greatly limited). Further detailed study, including the copolymerization in a preferential solvent, is now in progress and will be appear elsewhere.

REFERENCES

1. Y. Yamashita, *Appl. Polym. Symp.*, **36**, 193 (1981); *Kobunshi*, **31**, 988 (1982).
2. K. Ito, N. Usami, and Y. Yamashita, *Macromolecules*, **13**, 216 (1980).
3. T. Nishimura, M. Maeda, Y. Nitadori, and T. Tsuruta, *Makromol. Chem. Rapid. Commun.*, **180**, 1877 (1979).
4. R. Asami, M. Takaki, K. Kita, and E. Asakura, *Polym. Bull.*, **2**, 713 (1979); R. Asami, M. Takaki, K. Kyuda, and N. Sukenaga, *Polym. J.*, **15**, 261 (1983).
5. Y. Yamashita, Y. Tsukahara, K. Ito, K. Okada, and Y. Tajima, *Polym. Bull.*, **5**, 335 (1981).
6. Y. Kawakami, Y. Miki, T. Tsuda, R. A. N. Murphy, and Y. Yamashita, *Polym. J.*, **14**, 913 (1982).
7. Y. Tsukahara, K. Kohno, and Y. Yamashita, *Nippon Kagaku Kaishi*, 1070 (1985).
8. Y. Chujo, T. Shishino, Y. Tsukahara, and Y. Yamashita, *Polym. J.*, **17**, 133 (1985).
9. Y. Tsukahara, N. Hayashi, and Y. Yamashita, *Polym. Prepr. Jpn.*, **34**, 1453 (1985).
10. J. P. Kennedy and C. Y. Lo, *Polym. Bull.*, **8**, 63 (1982); *ibid.*, **13**, 343 (1985).
11. G. O. Schulz and R. Milkovich, *J. Polym. Sci., Polym. Chem. Ed.*, **22**, 1633 (1984).
12. K. Ito, H. Tsuchida, A. Hayashi, T. Kitano, E. Yamada, and T. Matsumoto, *Polym. J.*, **17**, 827 (1985).
13. K. Ito, H. Tsuchida, and T. Kitano, *Polym. Bull.*, **15**, 425 (1986).
14. G. G. Cameron and M. S. Chisholm, *Polymer*, **26**, 437 (1985); *ibid.*, **27**, 1420 (1986).
15. T. Otsu, T. Ito, and M. Imoto, *J. Polym. Sci., B*, **3**, 113 (1965).
16. J. Brandrup and E. H. Immergut, Ed., "Polymer Handbook," 2nd ed, John Wiley & Sons, New York, N. Y., 1975.
17. H. Morawetz, J. R. Cho, and P. J. Gans, *Macromolecules*, **6**, 624 (1973).
18. K. Horie, I. Mita, H. Kambe, *Polym. J.*, **4**, 341 (1973); K. Horie and I. Mita, *Macromolecules*, **11**, 1175 (1978).
19. T. Inoue, T. Soen, T. Hashimoto, and H. Kawai, *Macromolecules*, **3**, 87 (1970).
20. T. Hashimoto, M. Shibayama, and H. Kawai, *Macromolecules*, **13**, 1237 (1980).
21. T. Kotaka, Ed., "Polymer Alloys," Tokyo Kagaku Dohjin, Tokyo, 1981.
22. T. Kotaka, H. Ohnuma, and H. Inagaki, in "Colloid and Morphological Behavior of Block and Graft Copolymers," G. E. Molau, Ed., Plenum Press, New York, N. Y., 1971.
23. D. R. Paul and S. Newman, "Polymer Blends," Academic Press, New York, N. Y., 1978, Chapters 2 and 4.
24. G. Odian, "Principles of Polymerization," 2nd ed, John Wiley & Sons, New York, N. Y., 1981, Chapters 3 and 6.