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NOTES

Polymerization of Macromonomers IV. Monomer Reactivity Ratios in Radical Copolymerization of Methyl Methacrylate with (*p*-Vinylbenzyl)polystyrene Macromonomer

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Macromonomers have been recognized to be extremely useful for the preparation of novel multibranched (co-)polymers such as star, comb, and graft type (co-)polymers, as reviewed by many polymer chemists.[1]

For the construction of well-defined polymer architecture by such a macromonomer, fundamental data on homo- and/or copolymerization of the macromonomer are indispensable. In regard to copolymerizations of conventional small monomers (M_1) with macromonomers (M_2), monomer reactivity ratios of r_1 have been reported relatively extensively.[2-12] However, papers dealing with both r_1 and r_2 values have been limited.[13-18]

We previously[19] determined both r_1 and r_2 for a combination of 2-vinylnaphthalene and methacrylate-/acrylate-terminated poly(tetrahydrofuran) macromonomers using large difference in their extinction coefficients in the UV range.

In the present study, we evaluated both r_1 and r_2 values in the copolymerization of methyl methacrylate (M_1) with (*p*-vinylbenzyl)polystyrene macromonomer (M_2), by taking advantage of the high sensitivity of the carbonyl group of the small monomer to an IR spectrometer.

EXPERIMENTAL

Materials, Procedures, and Measurements

Two different molecular weights of VB–PSt macromonomers were prepared by a method reported previously.[20] The characterization results of the macromonomers are as follows.

$$\text{VB–PSt}_3:\ M_n = 3.0 \times 10^3,\quad M_w/M_n = 1.1_7,\quad f = 1.0$$

$$\text{VB–PSt}_6:\ M_n = 6.2 \times 10^3,\quad M_w/M_n = 1.0_5,\quad f = 0.97$$

^{13}C-Enriched MMA was synthesized from ^{13}C CH_3OH and methacryloyl chloride. The purity and ^{13}C-content of the monomer obtained after the fractional distillation were 88.2% and 22.3%, respectively. Commercially available MMA and α,α'-azobisisobutyronitrile (AIBN) were purified by the usual methods.

The procedures for the copolymerization of MMA with VB–PSt were the same as in the previous paper.[19]

Infrared (IR) spectra were recorded at a sufficiently slow scanning speed (20 min) for quantitative purposes on a JASCO A-102 spectrometer. ^{13}C NMR measurements were carried out in deuterochloroform solutions on

a Varian XL-200 spectrometer operated at 50 MHz. Gel permeation chromatographic (GPC) analysis was performed as reported previously.[19]

Determination of Composition of Copolymer

Owing to the narrow molecular weight distribution of VB–PSt, a GPC curve of recovered polymer after copolymerization gave good separation between the peaks of copolymer and unpolymerized VB–PSt. Thus, the extent of conversion of VB–PSt could be readily determined by the ratio of the area of the copolymer peak to the total response, because the contribution of the PMMA moiety to the copolymer peak area was negligibly small.

The extent of conversion of the small monomers was mainly determined by an IR method. The method was based on a calibration curve constructed by plotting the transmittance ratios of 1730 cm^{-1} (C=O) to 1875 cm^{-1} (benzene ring) against the mole ratios of PMMA monomer units to PSt monomer units. Some values determined by the IR method were checked by a ^{13}C NMR method involving a calibration curve. The curve was obtained by plotting the peak intensity ratios of methoxy carbons of ^{13}C-enriched MMA to the 1-carbons of benzene rings of polystyrene units against the mole ratios of PMMA monomer units to PSt monomer units.

The compositions of the copolymers were determined from the extents of both conversion of VB–PSt and small monomers determined according to the above method.

RESULTS AND DISCUSSION

Radical Copolymerization of VB–PSt Macromonomer

Typical results of the copolymerizations are summarized in Table I along with copolymerization conditions. The copolymer composition data by the IR method are consistent with those by the ^{13}C NMR method within experimental error. Figure 1 shows plots of monomer feed *vs.* copolymer composition and copolymerization composition curves drawn from the monomer reactivity ratios estimated by the intersection method. The experimental points are in fair agreement with the copolymer composition curves, supporting the validity of the values of monomer reactivity ratios. Also, Figure 1 illustrates the copolymerization reactivity of VB–PSt to decrease

Table I. Radical copolymerization of MMA (M_1) with VB–PSt (M_2)[a]

Run	M_1 mg	M_2 mg	Benzene mg	Time h	Conv. %	Mol% of M_2 in feed	Mol% of M_2 in copolymer
	MMA	VB–PSt_6					
1	21.7	151	254	0.3	17	10	13[c]
2	3.8	154	275	1.5	30	39	33[c]
3	2.1	184	340	2.5	20	59	46[c]
4	0.5	251	480	5.0	19	89	83[c]
	^{13}C MMA[b]	VB–PSt_3					
5	45.1	150	671	0.3	14	10	18[c]
6	15.2	150	704	0.7	15	25	30[c] (25)[d]
7	4.4	149	706	2.0	15	53	46[c] (43)[d]
8	3.0	201	951	2.5	15	69	66[c] (62)[d]

[a] Copolymerization conditions: temp, 60°C; solvent, benzene; $[M_2]_0 \approx 50$ mmol l^{-1}; $[AIBN]_0 \approx 20$ mmol l^{-1}.
[b] ^{13}C-enriched MMA.
[c] Determined by the IR method.
[d] Determined by the ^{13}C NMR method.

slightly with increase in the molecular weight of VB–PSt. These findings will be discussed in the following section.

Monomer Reactivity Ratio

Monomer reactivity ratios for the copolymerizations of MMA (M_1) with VB–PSt's (M_2) were estimated by both intersection and Fineman–Ross methods. The values are listed in Table II together with the literature values of monomer reactivity ratios in copolymerizations of MMA (M_1) with styrene[21] and with *p*-methylstyrene[22] (M_2) which can be regarded as model copolymerizations. In the copolymerization of VB–PSt having molecular weight of 6.2×10^3, the value of r_1 was about twice as large as that of the model copolymerizations, whereas the r_2 value was around half as small as that of the model copolymerizations. In the case of VB–PSt with molecular weight of 3.0×10^3, however, the value of r_1 was close to that of the model copolymerization while the r_2 value was similar to that in the case of VB–PSt with molecular weight of 6.2×10^3. These results may be interpreted in terms of polymer effect[23–27] and the concept[28] of equal reactivity of growing chains, as described in the previous paper.[19]

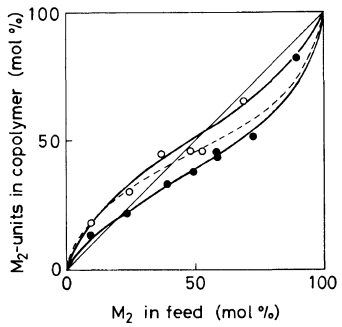

Figure 1. Copolymer composition curves for copolymerizations of MMA (M_1) with M_2 by AIBN at 60°C in benzene. M_2 = VB-PSt$_6$ (—●—), VB-PSt$_3$ (—○—), or St (----).

In the monomer reactivity ratios, $r_1 = k_{11}/k_{12}$ and $r_2 = k_{22}/k_{21}$, the rate constants for propagation reactions to low molecular weight monomer (*i.e.*, k_{11} and k_{21}) may be close to those for the model copolymerizations, because the concept of equal reactivity of growing chains is considered valid. On the other hand, the rate constants for propagation reactions to the macromonomer (*i.e.*, k_{12} and k_{22}) appear much lower than those for the model copolymerizations, because these propagations are concerned with polymer–polymer reactions. In reactions between polymers, it has been reported that the reaction rates are usually lower than those for an analogous small molecule reaction. For example, in anionic grafting reaction between polymers, hindering effect (kinetic excluded volume effect[27]) on reaction rates was observed for middle pendant functional groups of backbone polymer more significantly than those located near at chain ends.[25,26] In some cases[23,24] of bimolecular radical chain termination, the rate constant decreased by a factor of 100 or more. We recently found that star type and pine needle-shaped macromonomers,

Table II. Monomer reactivity ratio for the copolymerization of MMA with VB–PSt

M_1	M_2	mol. wt. $\times 10^{-3}$	r_1	$1/r_1$	r_2	Remarks
MMA	VB–PSt	6.2	0.89 (0.76)[a]	1.1 (1.3)[a]	0.22 (0.14)[a]	This work
^{13}C MMA[b]	VB–PSt	3.0	0.47 (0.44)[a]	2.1 (2.3)[a]	0.24 (0.18)[a]	This work
MMA	*p*-MSt	0.118	0.41	2.5	0.44	Ref 23
MMA	St	0.104	0.46	2.2	0.52	Ref 22

[a] By the Fineman–Ross method.
[b] ^{13}C-enriched MMA.

which have a functional group at the center of a polymer chain, are hardly homopolymerized by a radical initiator.[29] These findings on polymer effects on reaction rate suggest that the values of k_{22} and k_{12} for the copolymerization of VB–PSt are lower than those for the model copolymerization and that the extent of decrease in k_{22} is higher than that in k_{12} since k_{22} involves an α-branched polymer radical and a macromonomer molecule as reactants. The α-branch directly attached to a unit of a growing radical would cause the position of the growing radical to be in the middle of the polymer chain.

Consequently, the k_{22}/k_{21} (r_2) value for copolymerization of VB–PSt should be lower than that for the model copolymerization, whereas the k_{11}/k_{12} (r_1) value for the copolymerization of VB–PSt should be higher than that for the model copolymerization. In the case of VB–PSt_3, the r_1 value was almost comparable to that for the model copolymerization. This may be due to the slight hindering effect on the rate constant of k_{12} by a branch relatively short and the lower viscosity of copolymerization solutions of VB–PSt_3 than that of VB–PSt_6 solutions. The effect of viscosity has recently been found on the rate of macromonomer polymerization.[30]

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