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FREE-RADICAL POLYMERIZATION OF MACROMONOMERS

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ABSTRACT

Vinylbenzyl-terminated polystyrene (PS) macromonomers with various molecular weights were prepared by the direct reaction of living anion ends with *p*-chloromethylstyrene (CMS). The values of propagation rate constants (k_p) were obtained from free radical polymerizations of PS macromonomers in benzene at 40°C in the presence of 1-buten-3-ol as a degradative chain transfer agent by using gel permeation chromatography (GPC) analysis. The polymer radicals were terminated by a unimolecular mechanism. We studied the propagation step of PS macromonomers from the point of view of molecular weight dependences on the k_p .

INTRODUCTION

The importance of the synthesis of polymers with controlled molecular architecture has been increased due to the rising demands for new speciality polymers. Since Milkovich and Chiang [1–3] demonstrated the syntheses and applications of a variety of macromonomers, it has been established that the macromonomer technique is one of the best for the preparation of well-defined graft copolymers. Macromonomers can be defined as polymers endcapped with a polymerizable functional group at the chain end. Homopolymerization systems of macromonomers exhibit the following features in comparison with polymerization systems of small monomers [4, 5]: 1) high viscosity of the polymerization media from the beginning of

polymerization, 2) low molar concentration of macromonomers, 3) the propagating step is the polymer-polymer reaction, and 4) high segment density around the propagation radical sites due to multibranched structure. It is therefore of interest to determine the kinetics in the free-radical polymerization of macromonomers.

In comparison with small monomers, the molar concentration of macromonomers is usually very low, even in bulk concentration, so the conventional dilatometric method cannot be utilized to pursue polymerization kinetics. Tsukahara et al. [5] recently reported that the electron spin resonance spectroscopy (ESR) spectra of the propagating radical of polystyrene (PS) macromonomers were measured to evaluate the concentration of the propagating radicals. From the results of ESR and gel permeation chromatography with a laser light-scattering detector (LS-GPC), the propagation rate constant k_p , the termination rate constant k_t , and the radical lifetime τ_p of the macromonomers were evaluated. A long time ago we established an estimation method for the rate constants of intramolecular and intermolecular crosslinkings from kinetic analysis by using a soluble microgel with several pendant vinyl groups by assuming a unimolecular termination mechanism of polymer radicals [6-8]. The rate constant of intermolecular crosslinking was estimated by GPC analysis on the polymer produced from intermolecular propagation between dimers. On the basis of this concept, we have synthesized PS, polyvinyl acetate, and polymethacrylate macromonomers by the radical polymerization of each monomer initiated by a functional azo-initiator in the presence of allylmalonic acid diethylester as a degradative chain transfer agent, followed by an end-capping reaction with *p*-chloromethylstyrene (CMS) [9, 10].

For this article, vinylbenzyl-terminated PS macromonomers with various molecular weights were made by the direct reaction of living anion ends with CMS. The k_p values were obtained from free-radical polymerizations of PS macromonomers in benzene at 40°C in the presence of 1-buten-3-ol as a degradative chain transfer agent by using GPC analysis. We discuss the propagation step of PS macromonomers from the point of view of molecular weight dependence of k_p .

EXPERIMENTAL

Synthesis and Characterization of PS Macromonomers

Vinylbenzyl-terminated PS macromonomers were synthesized by the coupling reaction of polystyryl anion initiated by *n*-butyllithium (*n*-BuLi) with an excess amount of CMS in a benzene-tetrahydrofuran (THF) mixed solvent [11,12]. Styrene and CMS (from Seimi Chemical Ind. Ltd.) monomers were dried over a mixture of calcium hydride-lithium aluminum hydride and then distilled under vacuum. Subsequently, styrene was purified with triphenylmethyl sodium in vacuum. Benzene was dried over sodium metal and then purified with *n*-BuLi under vacuum. THF was distilled from its solution of α -methylstyrene tetramer sodium anion under vacuum. The product was purified three times by reprecipitation from benzene solution with methanol.

The number-average molecular weight (\bar{M}_n) of PS macromonomers was determined by GPC (Tosoh high-speed liquid chromatograph HLC-8020) with THF as eluent at 38°C, a TSK gel GMH_{XL} column, and a flow rate of 1.0 mL/min using a calibration curve of standard PS samples. The \bar{M}_n of PS with lower molecular

weights was determined by vapor pressure osmometry on a Corona NA 117 vapor pressure osmometer in benzene. The polydispersity ($\overline{M}_w/\overline{M}_n$) was determined from GPC distribution functions improved by the reshaping method [13] with a personal computer. The content of terminal vinylbenzyl groups was determined by the area ratio of refractive index (RI) and UV (292 nm) intensities on a GPC chart (by a calibration curve constructed from a mixture of PS and *p*-methylstyrene) [12]. The characteristics of PS macromonomers used are listed in Table 1.

Radical Polymerization of PS Macromonomers

Tsukahara et al. [4] investigated the radical polymerization behavior of PS macromonomers. They made it clear that the \overline{M}_w of branched PS formed was very small at macromonomer concentration [PM] less than ca. 2×10^{-2} mol/L. Beyond this concentration, the molecular weight of branched PS rapidly increased to a great extent with an increase of [PM]. So the feed concentration of macromonomer was set up according to the above results. PS macromonomer, 2,2-azobis(4-methoxy-2,4-dimethylvaleronitrile) as an initiator (V-70; Wako Pure Chemical Ind. Ltd.), 1-buten-3-ol, and benzene were charged in a polymerization ampule and sealed off under high vacuum. This ampule was set in thermostated baths of 40°C. After the reaction time, each reaction solution was terminated with a small amount of hydroquinone. The product was recovered by reprecipitation with methanol. The molecular weight distribution of each product was measured by GPC. These distribution functions were improved by the reshaping method.

Analysis of Polymerization Systems

The free-radical polymerization of macromonomers accompanied with a unimolecular termination is expressed as follows, assuming that the terminal vinylbenzyl groups of macromonomers are distributed at random in the polymerization solution. The reaction condition in which only dimer is formed in this system is chosen. A possible mechanism for the polymerization of PS macromonomer radical (PM_i^{\cdot}) is:

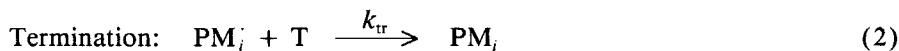
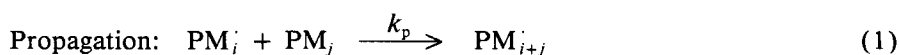


TABLE 1. Characteristics of PS Macromonomers

Code	$\overline{M}_n \times 10^{-4}$ ^a	$\overline{M}_w/\overline{M}_n$ ^a	Vinylbenzyl group ^b (number/1-polymer)
SM1	1.29	1.08	1.02
SM2	2.93	1.09	1.10
SM3	4.20	1.06	0.86
SM4	6.98	1.11	0.92

^aDetermined by GPC.

^bDetermined by GPC with RI and UV double detectors.

where PM_i and PM_j are terminal vinylbenzyl groups belonging to the i - and j -macromonomer species, respectively. T and k_{tr} are the degradative chain transfer agent and the rate constant of termination, respectively. Allyl radicals produced from Eq. (2) are stabilized by resonance structures. Therefore, these radicals are not able to attack the macromonomers. The consumption rates of PM^\cdot and initiator radical (I^\cdot) are given as follows, respectively:

$$d[PM^\cdot]/dt = k_i[I^\cdot][PM] - k_{tr}[PM^\cdot][T] \quad (3)$$

$$d[I^\cdot]/dt = 2fk_d[I] - k_i[I^\cdot][PM] \quad (4)$$

where k_i and k_d are rate constants of initiation and initiator decomposition, respectively. The factor f is termed the initiator efficiency and is included in the rate expression to take account of the fact that not all of the radicals produced initiate a chain. Reduced efficiency is attributed to cage effects in which radicals formed in the initiation reaction have a finite probability of recombining before they can diffuse through the cage of surrounding liquid molecules and initiate polymerization. Moreover, f is included in the rate expression for radical I^\cdot attacking T in this reaction system.

From the assumption of steady-state ($R_i = R_t$), $[PM^\cdot]$ is given by

$$[PM^\cdot] = 2fk_d[I]/k_{tr}[T] \quad (5)$$

Then the propagation rate is given by

$$R_p = k_p[PM_i][PM_j] \quad (6)$$

The rate constant k_p can be estimated from Eqs. (5) and (6) as follows:

$$k_p = R_p k_{tr}[T]/R_i[PM] \quad (7)$$

where $R_i = 2fk_d[I]$.

When R_i , k_{tr} , $[T]$, and $[PM]$ are known values, k_p can be calculated from Eq. (7) by measurement of R_p . R_p is estimated by GPC analysis of the dimers produced from the propagation reaction. Figure 1 shows a schematic representation of the reshaped GPC profile of the polymerization product. P_1 and P_2 are unimolecular termination (containing unpolymerized macromonomer) and dimer products, respectively. P_2 can be separated from the reshaped GPC of the polymerization product by subtracting the known distribution function of P_1 on a personal computer. The w_1 and w_2 are weight fractions of P_1 and P_2 , respectively. The molecular numbers of P_1 (n_1) and P_2 (n_2) are given by

$$n_1 = w_1/M_1 \quad \text{and} \quad n_2 = w_2/2M_1 \quad (i = j) \quad (8)$$

where M_1 is the M_n of the starting PS macromonomer.

The $(n_1 + 2n_2)$ is equal to the feed molecular number of macromonomer, and its material balance is constant before and after the propagation reaction. Then R_p is estimated from the relationship between the yield of P_2 and time.

Measurements of R_i and k_{tr}

Both values were measured in a previous report [8]. In brief, the value of R_i was measured by using the 2,2,6,6-tetramethyl piperidinyloxy free radical (TEMPO) as follows. The radical polymerization of styrene was carried out in

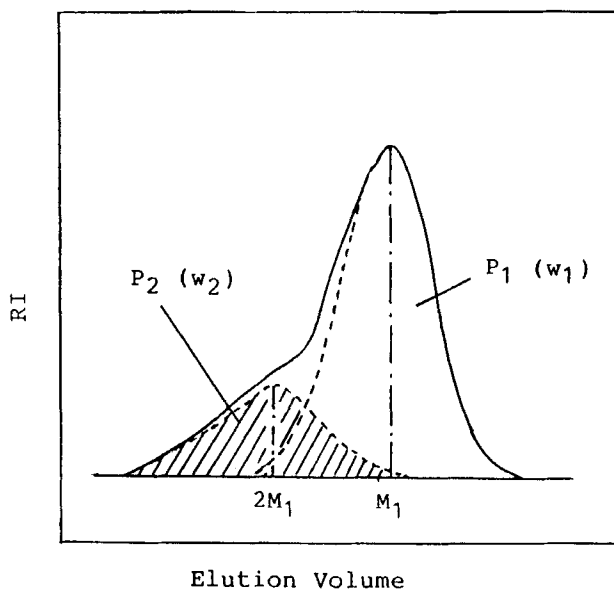


FIG. 1. Schematic representation of GPC profile of polymerization product: P_1 , unimolecular termination product (containing unpolymerized macromonomer); P_2 , dimer; w_1 , weight fraction of P_1 ; w_2 , weight fraction of P_2 ; M_1 , \bar{M}_n of starting macromonomer.

benzene initiated by V-70 at 40°C in the presence of TEMPO. The initial time of consumption of the terminal vinylbenzyl groups was measured photometrically at 292 nm. R_i was determined to be 1.81×10^{-7} mol/L·s ($[I]_0 = 0.02$ mol/L) from the relationship of induction periods and the TEMPO feed. The transfer constant of 1-buten-3-ol (40°C) was estimated from the results of the homopolymerization of styrene to be 2.38×10^{-3} , and the value of k_{tr} was 0.331 L/mol·s.

RESULTS AND DISCUSSION

Table 1 lists the characteristics of vinylbenzyl-terminated PS macromonomers. The conversion was almost 100% within experimental error in all macromonomer syntheses. The GPC profiles showed that SM macromonomers had a single and relatively narrow molecular weight distribution. The direct coupling of polystyryl anion with CMS formed the PS macromonomer possessing one vinylbenzyl group at the terminal end.

Figure 2 shows typical reshaped GPC profiles of SM2-1 ($[PM]_0 = 0.04$ mol/L, $[I]_0 = 0.02$ mol/L, $[T]_0 = 0.46$ mol/L) for changing polymerization times (10–50 hours). Under these polymerization conditions, the trimer is scarcely formed. It is speculated from these results that the reactivity of dimer radical is extremely low compared to that of unimer radical. We could not estimate the conversion of macromonomer from these GPC profiles with a RI detector because unimer radical attacks competitively the macromonomer (dimer radical information) and degradative transfer agent. The distribution of P_1 at the lower elution volume was the same

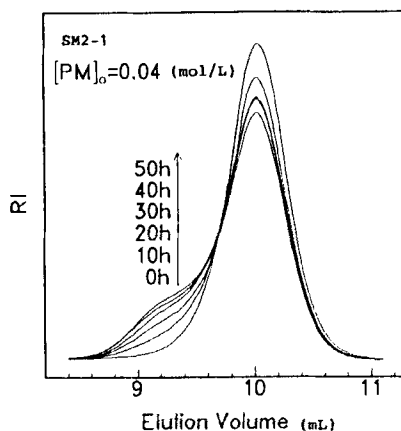


FIG. 2. Typical GPC profiles of SM2-1 changing polymerization time.

as that of the original SM2 macromonomer. The amounts of dimer P_2 produced increase with increasing polymerization time. After separation of P_2 distributions by simulation using a personal computer, the yield of P_2 was estimated as shown in Table 2. Figure 3 shows the relationship between the yield of P_2 and the polymerization time for SM2-1. From this curve, the value of R_p is estimated to be 1.5×10^{-7} (mol/L·s).

The polymerization conditions and numerical values to estimate k_p for SM macromonomers are listed in Table 3. The SM1-1 to SM4-1 and SM2-0 to SM2-2 series correspond to experiments for studying the dependence of molecular weight and concentration of macromonomers, respectively. It is found from the results of the SM2-0 to SM2-2 series that k_p increases gradually with increasing feed macromonomer concentration $[PM]$. Tsukahara et al. [4] reported that radical polymerization of macromonomers scarcely proceeded at $[PM]_0$ less than 0.016 mol/L. Beyond this concentration, the molecular weight rapidly increased with an increase of $[PM]$. In our work, the polymerization of PS macromonomers also scarcely proceeded at less than ca. 0.02 mol/L of $[PM]_0$. The k_p seems to depend slightly upon the macromonomer concentration in the feed.

Our results show that k_p has an almost constant value (1–3 L/mol·s) in the \overline{DP} range of 124–670 of PS macromonomers. According to Tsukahara's study [5], the k_p of the vinylbenzyl-terminated PS macromonomer ($DP = 48$) at 60°C was 5

TABLE 2. Yield of P_2 for Polymerization SM2-1^a

Code	Yield of P_2 (wt%) for different times (in hours)				
	10	20	30	40	50
SM2-1	11.3	15.5	20.3	20.4	21.0

^aEstimated from the GPC profile of each polymerization product.

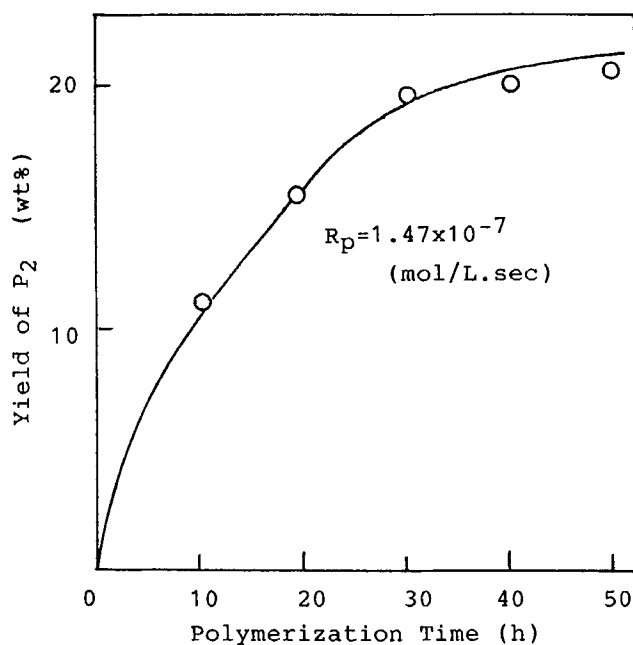


FIG. 3. Relationship between the yield of P₂ and the polymerization time for SM2-1.

TABLE 3. Polymerization Conditions and Results of Free-Radical Polymerizations^a

Expt.	Macromonomer			$R_p \times 10^8$ mol/L·s	k_p , L/mol·s
	[PM] ₀ , mol/L	Polymer conc, wt%	\overline{DP}^b		
SM1-1	0.04	36.7	124	3.80	1.0 ± 0.2
SM2-1	0.04	53.6	281	14.0	3.0 ± 0.1
SM3-1	0.04	70.1	403	9.40	2.0 ± 0.1
SM4-1	0.04	77.6	670	7.02	1.0 ± 0.3
SM2-0	0.02	36.6	281	3.27	1.0 ± 0.3
SM2-1	0.04	53.6	281	14.0	3.0 ± 0.1
SM2-2	0.06	63.4	281	25.0	4.0 ± 0.5

^aPolymerized in benzene at 40°C; [T]₀ = 0.46 mol/L, [I]₀ = 0.02 mol/L.

^bDegree of polymerization.

L/mol·s. On the other hand, the k_p for the free-radical polymerization of styrene ($\overline{DP} = 1$) is 139 L/mol·s at 40°C [14]. It was found that k_p decreases rapidly at $\overline{DP} = \text{ca. } 50$ or more of macromonomers. The propagation step of macromonomers depends strongly upon the molecular weight because of the high viscosity of the polymerization media. It is necessary to accumulate the kinetic data in the lower \overline{DP} range (ca. 10).

We are investigating free-radical polymerization in micelles formed by diblock macromonomer (organized polymerization). The information obtained will make clear the effect of reaction fields on k_p and will be reported shortly.

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