Macromolecules 1989, *22*, 2869-2871

(12) Jasse, B.; Monnerie, L. *J. Mol. Struct.* 1977, *39*, 165.

Nicholas M. Reynolds, John D. Savage, and Shaw Ling Hsu*

Polymer Science and Engineering Department and Chemistry Department, University of Massachusetts Amherst, Massachusetts 01003

Received February 16, 1989;
Revised Manuscript Received April 10, 1989

On the Propagating Radical of Macromonomers

Recently, the number of studies on the synthesis and application of macromonomers has been rapidly increasing since macromonomers are very useful in the preparation of various kinds of functional graft copolymers having well-defined structure.[1-3] However, polymerization as well as copolymerization behavior of macromonomers is not yet well understood.[4-6] In comparison with small monomers, the polymerization system of macromonomers has the following characteristic features: (i) the viscosity of polymerization media is high from the beginning of polymerization, (ii) the concentration of the polymerizable end group is low, (iii) the propagating step is repeat of polymer–polymer reaction, and (iv) the segment density or multibranched structure is high around the propagating radical site. These features suggest that the polymerization of macromonomers might be unusually sensitive to the diffusion-controlled step of the polymerization reaction. Therefore, it is very interesting and worthwhile to investigate the polymerization behavior of macromonomers to understand how the diffusion-controlled step influences the chemically-controlled nature of polymerization reaction in general.

In the previous paper,[5] we reported that the specific features of the polymerization system of macromomomers mentioned above strongly influences the radical polymerization behavior. It was shown that there is a unique dependence of the degrees of polymerization (Dp) and the apparent kinetic order of the polymerization upon the feed macromonomer concentration [M] and the initiator concentration [I] and this requires further investigations.

In this study, we intended to investigate the polymerization behavior of macromonomers by means of ESR spectra in order to obtain direct information about the propagating macromonomer radicals. ESR measurements on the propagating radicals in solution polymerization of the small monomers are difficult to obtain because the concentration of the radicals is too low. Thus, the use of ESR spectra is limited to polymerization systems in highly viscous solution or in bulk.[7,8] However, in macromonomer systems, the propagating radicals are expected to be stable and accordingly detectable by ESR, because of the specific feature of the macromonomer polymerization system mentioned above.

The macromonomer used is the same as that in the previous paper,[5] that is, a styrene macromonomer having a methacryloyl end group that was prepared by deactivation of polystyryl living anion with ethylene oxide, followed by the reaction with methacryloyl chloride. The number-average molecular weight (M_n) is 1.24×10^4 and polydispersity index (M_w/M_n) is 1.06. The macromonomer, AIBN, and benzene were carefully placed in the ESR sample tube, degassed, and sealed under high vacuum. ESR measurements were carried out during the polymerization reaction with a JEOL ME-3X X-band spectrometer with 100-kHz modulation.[9,10] The signal of diphenylpicrylhydrazyl (DPPH) was used as a g value standard. The magnetic field sweep was calibrated with the splitting constant of Mn^{2+}. The concentrations of macromonomer [M] and initiator [I] are shown in Table I. In the case of run d in Table I, a mixture of MMA monomer and inert PSt standard (number-average molecular weight 1.0×10^4, $M_w/M_n = 1.06$) was used instead of the macromonomer. In this case, the vinyl end group of macromonomer becomes separated from its tail or remaining part (polymerization of MMA in the presence of PSt).

Table I
Polymerization Systems of Methacryloyl-Ended St Macromonomer and MMA/PSt Mixture for ESR Measurement[a]

run	monomer	[M], 10^{-2} mol/L	[I], 10^{-2} mol/L
a	St macromonomer	1.1	16.4
b	St macromonomer	4.0	1.6
c	St macromonomer	4.0	16.4
d	MMA + PSt	4.0	16.4

[a] ESR measurements were carried out during the polymerization.

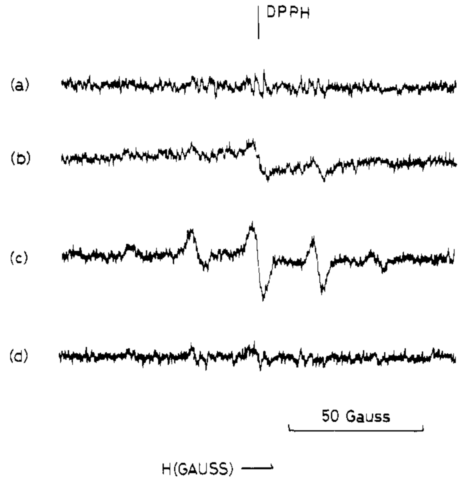

Figure 1. ESR spectra measured during polymerization of the macromonomer. Polymerization temperature was 60 °C in all cases: (a) [M] = 1.1×10^{-2} mol/L, [I] = 1.6×10^{-1} mol/L; (b) [M] = 4.0×10^{-2} mol/L, [I] = 1.6×10^{-2} mol/L; (c) [M] = 4.0×10^{-2} mol/L, [I] = 1.6×10^{-1} mol/L; (d) [M] = 4.0×10^{-2} mol/L, [I] = 1.6×10^{-1} mol/L. Sweep time is 4 min, response time is 0.1 s. The vertical line in the figure is DPPH, $g = 2.0036$.

Typical examples of ESR spectra are shown in Figure 1. It is seen that there is a broad five-line spectrum in run (b) and that the signal becomes more clear in run (c), as another weak four-line spectrum seems to superimpose to give the nine-line spectrum. This spectrum becomes sharper at −196 °C, as shown in Figure 2(ii) and it is almost identical with that of the spectrum of the MMA propagating radical in the literature,[7,8,12,13] which is characterized by nine lines consisting of five strong lines having a hyperfine splitting constant of 23.4 G (intensity distribution is 1:4:6:4:1) and of four weak lines, appearing between the five lines. On the other hand, there is no clear signal from the radical in spectra (a) and (d) other than the small signals ascribed to cyanoisopropyl radicals arising from AIBN.[7,11] In Figure 1(a), [M] decreases to 1.1×10^{-2} mol/L but [I] is the same as that in (c). This macromonomer concentration is not high enough to produce the poly(macromonomer) of large Dp as shown in Figure 3 in a previous paper. The signal cannot be observed in Figure 1(d) either, where the polymerizable end group is separated from the remaining part of the macromonomer. These

0024-9297/89/2222-2869$01.50/0

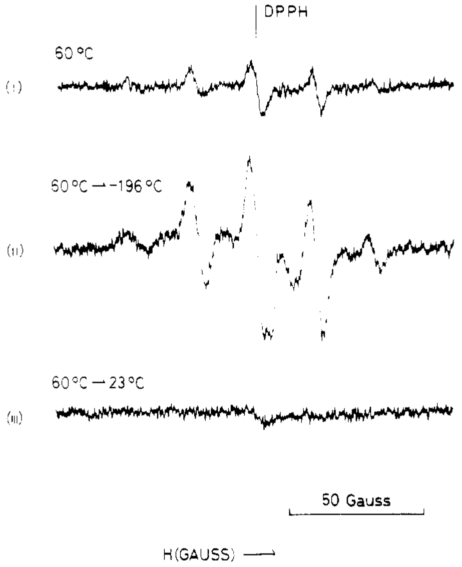

Figure 2. Change of ESR spectra of (c) in Figure 1 by quenching and aging: (i) 60 °C at 3 h; (ii) −196 °C, measured at ca. 20 min after (i); (iii) room temperature, measured at ca. 20 min after (ii). In the case of (ii), sweep time is 16 min and response time is 1 s, and the conditions are same as in Figure 1 in other cases.

results indicate that the ESR spectra in Figure 1(b),(c) and Figure 2(ii) can be attributed to the propagating radical of the macromonomer.

The differences between spectra (b), (c) and (a), (d) are due to considerable differences in stability and concentration of the propagating radicals. That is, in the case of (a), both the gel effect (Trommsdorf effect) and the segment density around the propagating radical site are not high enough to decrease the termination reaction rate sufficiently.[5] Thus, the radical concentration is too low for ESR measurement. In case (d), the viscosity is almost the same as that of (b) and (c), due to the presence of the inert PSt (the molecular weight of which is almost the same as that of the macromonomer). However, the propagating chain is linear and the radical site is located at the chain end, as in the systems of small monomers, where the propagating radical has sufficient mobility. Therefore, bimolecular termination reaction occurs without difficulty, and the radical concentration in (d) is too low to be detected. This indicates that the stability and increased concentration of the propagating radical of macromonomer can be ascribed to the specific multibranched structure of the propagating species. In this case, the segmental motion of the radical site always requires dragging neighboring branch segments. Consequently, the rate of termination reaction of this radical is considerably decreased.

The change of spectrum c by quenching is shown in Figure 2. Spectrum (i) was taken at 60 °C, 3 h after the sample setting, (ii) was taken after quenching from 60 °C to liquid N_2 temperature (time interval between quenching and the measurement is ca. 20 min), and (iii) was taken at room temperature after quenching from 60 to 0 °C (the time interval is ca. 20 min). The nine-line ESR signal of the propagating radical was continuously observed for several hours at 60 °C during the polymerization. It is seen from Figure 2 that the radicals can be frozen in by quenching to −196 °C. The signal then becomes much sharper, as compared to those taken during polymerization. This is due to the increase in sensitivity at low temperature and to the increase in response time and sweep time. However, the signal became small and almost vanishes at 0 °C or at room temperature.

Table II
Propagating Rate Constant k_p for MMA Polymerization

k_p, L/mol·s	method	polymeriztn conditn	ref
37 (44)[a]	ESR	Bz, AIBN, 60 °C (macromonomer)	this work
720[b]	ESR	bulk, PO,[d] 60 °C	14
187	ESR	Bz,[e] UV, 30 °C	15
790[c]	ESR	emulsion, 50 °C, W_p = 0.5	16
260	rotating sector	Bz,[f] 25 °C	17

[a] Value in the parenthesis is corrected by the end functionality (f = 0.86). [b] From $k_p = 2.5 \times 10^6 \exp(-5400/RT)$. [c] From $k_p = 790 \exp[29.8(W_p - 0.84)]$ (for $W_p > 0.84$), $k_p = 790$ (for $W_p < 0.84$). [d] Initiator: dibenzoyl peroxide and cyclohexyloxycarbonyl peroxide. [e] MMA/Bz = 1/1 (v/v). [f] [M] = 4.69 mol/L.

From the ESR signal, the concentration of the propagating radical of macromonomer [M*] can be evaluated by comparing the signal to that from the standard containing a known concentration of DPPH. Then the propagating rate constant, k_p, the termination rate constant, k_t, and the radical life time, τ, can be directly determined with [M*] and Dp by the following relation:[8,14]

$$-\mathrm{d}[M]/\mathrm{d}t = k_p[M^*][M] \tag{1}$$

$$k_t = (-\mathrm{d}[M]/\mathrm{d}t)(1/\mathrm{Dp}[M^*]^2) \tag{2}$$

$$\tau = \mathrm{Dp}/k_p[M] \tag{3}$$

Obtained value of [M*] from the signal at −196 °C was 3.3×10^{-6} mol/L at [M] = 4.0×10^{-2} mol/L and [I] = 1.6×10^{-1} mol/L. By using this value, k_p, k_t, and τ were determined as 37 L/mol·s (44 L/mol·s after correction of the end functionality), 7600 L/mol·s, and 40 s, respectively, with Dp = 60 at this polymerization condition. The k_p value thus obtained was compared with those of the polymerization of MMA monomers, which are shown in Table II. In addition to the small value of k_t compared to that of the MMA monomer, it is seen from this table that k_p is also considerably decreased in the macromonomer system at this polymerization condition. This is clearly due to the high viscosity of polymerization media and the specific multibranched structure of the propagating radicals.

It is concluded from these findings that the propagating radical of the macromonomer is quite stable and detectable by ESR spectroscopy during solution polymerization at 60 °C, which can be frozen in at −196 °C by quenching to give the radical concentration. This is quite different from the polymerization of small monomers corresponding to the polymerizable end group of the macromonomer (MMA), where the detection of the propagating radical was difficult under the same condition. It was also shown that the rate constants for propagation and termination and the radical lifetime in the macromonomer system can be directly evaluated by measuring the concentration of the propagating radical with ESR spectrum. This information is very important and useful in understanding the polymerization behavior of macromonomers in detail because the polymerization behavior of macromonomers has been so far discussed only by the polymerization rate R_p. There have been no discussions about k_p and k_t. Further study on the polymerization of macromonomers is now in progress and will appear elsewhere.

Acknowledgment. This research was supported in part by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture, Japan (63750866).

References and Notes

(1) Yamashita, Y.; Tsukahara, Y. In *Modification of Polymers*; Carraher, C., Moore, J., Eds.; Plenum Press: New York, 1983; p 131.

(2) Rempp, P. F.; Franta, E. *Adv. Polym. Sci.* **1984**, *58*, 1.
(3) Tsukahara, Y.; Tsai, H-C.; Yamashita, Y.; Muroga, Y. *Polym. J.* **1987**, *19*, 1033.
(4) Asami, R.; Takaki, M.; Kyuda, K.; Sukenaga, N. *Polym. J.* **1983**, *15*, 261.
(5) Tsukahara, Y.; Mizuno, K.; Segawa, A.; Yamashita, Y. *Macromolecules* **1989**, *22*, 1546.
(6) Tsukahara, Y.; Tanaka, M.; Yamashita, Y. *Polym. J.* **1987**, *19*, 1121.
(7) Ranby, B.; Rabek, J. F. *ESR Spectroscopy in Polymer Research*; Springer-Verlag: Berlin, Heidelberg, New York, 1977.
(8) Kamachi, M. *Adv. Polym. Sci.* **1987**, *82*, 207.
(9) Kashiwabara, H.; Shimada, S.; Hori, Y.; Sakaguchi, M. *Adv. Polym. Sci.* **1987**, *82*, 141.
(10) Shimada, S.; Hori, Y.; Kashiwabara, H. *Macromolecules* **1988**, *21*, 2107.
(11) Bullock, A. T.; Burnett, G. M.; Kerr, C. M. L. *Eur. Polym. J.* **1971**, *7*, 1011.
(12) Komatsu, T.; Seguchi, T.; Kashiwabara, H.; Sohma, J. *J. Polym. Sci.* **1967**, *C16*, 535.
(13) Gillbro, T.; Yamaoka, H.; Okamura, S. *J. Phys. Chem.* **1973**, *77*, 1163.
(14) Bresler, S. E.; Kazbekov, E. N.; Shadrin, V. N. *Makromol. Chem.* **1974**, *175*, 2875.
(15) Kamachi, M.; Kohno, M.; Kuwae, Y.; Nozakura S. *Polym. J.* **1982**, *14*, 749.
(16) Ballard, M.; Gilbert R.; Napper D.; Pomery, P.; O'Sullivan W.; O'Donnell H. *Macromolecules* **1986**, *19*, 1303.
(17) Bamford, C. H.; Brumby S. *Makromol. Chem.* **1967**, *105*, 122.

Yasuhisa Tsukahara,* Kiyoharu Tsutsumi, and Yuya Yamashita
Department of Synthetic Chemistry
Faculty of Engineering, Nagoya University
Nagoya 464, Japan

Shigetaka Shimada
Nagoya Institute of Technology, Nagoya 466, Japan

Received February 8, 1989;
Revised Manuscript Received April 21, 1989

Scaling Behavior of Pregel Sols Obtained by End-Linking of Linear Chains

The sol–gel transition has been the subject of many theoretical and experimental studies in the last 50 years.[1-5] From a fundamental point of view, the universal features related to the transformation of the viscous reaction bath into an elastic solid are quite fascinating. From a more practical point of view, these universal features seem to be very useful to explain some of the properties of the final gel.[6]

To describe the sol phase before the gel point, the fundamental quantity is the size distribution function (SDF) of the species in the reaction bath.[1,3,7] It has been shown recently that size-exclusion chromatography (SEC) experiments provide a direct measurement of this function.[8-10]

Up to now, two different gelling reactions have been investigated with this technique: irradiation-induced random cross-linking of linear polystyrene (PS) solutions in θ conditions[8,9] and bulk condensation polymerization leading to a polyester network.[10] Although the two systems are quite different, the characterization of their sol phase before the gel point gave similar results. In both cases the experimental distribution functions are found to obey a scaling form. Also the values of the exponent τ, that characterizes the decay of the SDF at the gel point, are in good agreement with each other.

The purpose of this note is to describe preliminary results obtained with the SEC technique on a third and different system: end-linking of poly(dimethylsiloxane) (PDMS) chains in the melt. The results are shown to be consistent with those obtained with the two previous systems.

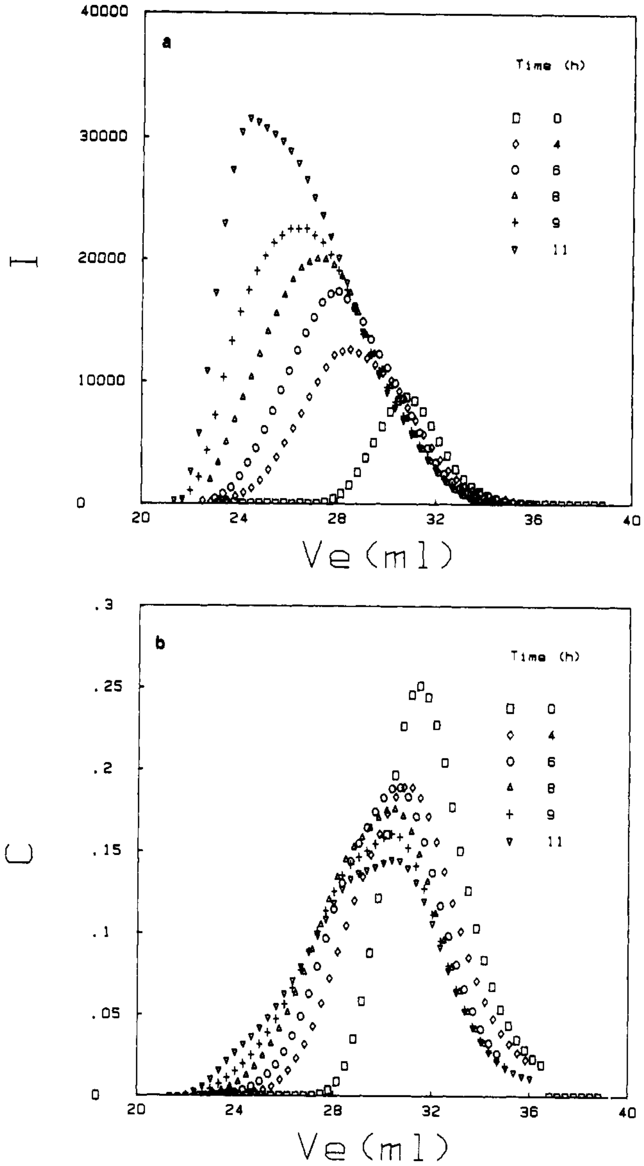

Figure 1. (a) Refractometry chromatograms for samples with different reaction times. The curves are normalized to a unit area. (b) Light-scattering chromatograms of the samples in (a). The curves are normalized so that the area is proportional to the weight-average molecular weight of the samples.

The precursor α,ω-functional linear chains are PDMS chains ($M_{w,0} \simeq 27000$) with dimethylsilyl groups at the ends. These chains are heated at 70 °C with tetrakis(allyloxy)ethane at a 1/1 stoichiometric ratio of dimethylsilyl to unsaturated functions, in the presence of chloroplatinic catalyst.[11] Samples are removed from the reaction bath at different reaction times and the reaction is stopped by using Rosenmund's poison.[12] Under these experimental conditions, we expect that the main reaction is the end-linking of the preexisting chains by the tetrafunctional units, with no influence of side reactions.[11] Thus branched molecules are obtained with a fixed length between cross-linking points.

Once the reaction is stopped, the samples are diluted in toluene and characterized by SEC coupled on line with a SHODEX SE11 refractometer and a home-built light-scattering apparatus.[13] The light source is a He–Ne laser and the scattering angle is 90°.

Figure 1 shows the evolution of the refractometry (a) and light-scattering signals (b) as the reaction time increases.

0024-9297/89/2222-2871$01.50/0