Notes

An ESR Study of Reversible Addition−Fragmentation Chain Transfer Copolymerization of Styrene and Maleic Anhydride

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It is well-known that the copolymerization of styrene (St) with maleic anhydride (MAn) via conventional radical technique is capable of providing an alternating copolymer easily.[1] However, the molecular weight and molecular weight distribution (M_w/M_n) of the copolymer thus obtained have not been well-defined. Recent demonstration solved the problem by employing reversible addition−fragmentation chain transfer (RAFT)[2] or nitroxide-mediated polymerization for the alternative copolymerizations.[3] By varying the feed ratios of St and MAn, a series of copolymer P(MAn-*alt*-St)$_m$-*b*-PSt$_n$ with different *m* and *n* were prepared via RAFT copolymerization. The hydrolyzed products of the copolymers showed self-aggregated uniform nanoparticle feature in an atomic force microscopy (AFM) image.[2a]

The mechanism of alternating radical copolymerization of St and MAn has provoked a great deal of controversy.[4] There are mainly two different mechanistic rationales of chain propagation: charge-transfer complex (CTC) model and polar transition state (or free monomer) model.[5] In the previous paper, we discussed that CTC formation of St and MAn favorably took place at the lower polymerization temperature of 60 °C. However, structures of the propagating species were still unknown.

Electron spin resonance (ESR) spectroscopy is a very powerful tool for the investigation of radical polymerization.[6] The concentrations of nitroxide free radicals in nitroxide-mediated polymerization of styrene[7] and the concentrations of copper(II) species in atom transfer radical polymerization (ATRP) systems[8] were determined by ESR measurements; thus, the kinetics was explored. Furthermore, ESR spectroscopy had been used to reveal the mechanism of RAFT polymerization of styrene and *n*-butyl acrylate by Hawthorne et al.[9] The presence of intermediate radical species formed by a series of reversible addition−fragmentation steps had been observed. However, line widths of the ESR spectra were too broad to determine detailed structures of the radicals. Recent development of ESR spectroscopy can greatly improve the spectra resolution under appropriate conditions and provide detailed information on structures of the radicals, which in turn may help to understand the mechanism of the polymerization processes.[6,10] In this note, ESR spectroscopy of the RAFT copolymerization of St and MAn was applied in order to clarify the nature of the propagating radical attached to the RAFT agent.

The sample solution in benzene containing purified monomers (St and/or MAn), dimethyl 2,2′-azobis(isobutyrate) (MAIB, as an initiator), and benzyl dithiobenzoate (BTBA, as a RAFT agent) was placed in a quartz ESR tube and purged with nitrogen for 5 min just prior to measurements. ESR spectra were recorded with a JEOL JES RE-2X spectrometer, using a universal X-band cavity, 100 kHz field modulation, with 0.32 G amplitude, and 1 mW microwave power. Measurement temperatures were controlled with JEOL DVT2 variable temperature unit. UV light was irradiated by a Ushio USD500D (500 W) ultrahigh-pressure mercury lamp equipped with an IRA25S infrared cutoff filter (Toshiba). The filter can cut infrared and UV light. Data acquisition, analysis, and spectral simulations were performed with the JEOL ESPRIT 330 data analysis system. Simulation with chemical exchange phenomena was performed by simulation program prepared by Rockenbauer.[11]

In conventional radical copolymerization of St and MAn, the polymerization rate was so fast that the detected ESR spectra were too complicated to interpret the structures of propagating radicals. In the presence of a RAFT agent, however, the chain propagating rate would be greatly reduced due to the formation of a relatively stable α,α-dialkylthiobenzyl radical which can be easily detected. Structures of propagating radicals could be deduced from the ESR spectra if well-resolved signals could be obtained. According to the literature,[9] there should be three possible intermediate radicals during the RAFT copolymerization of St and MAn, as shown in Scheme 1. To clarify which of the structures of radicals dominates in the RAFT copolymerization of St and MAn, RAFT homopolymerization of styrene and

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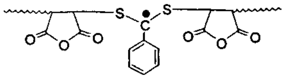
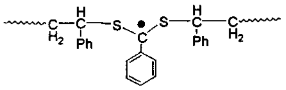
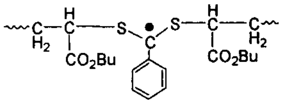
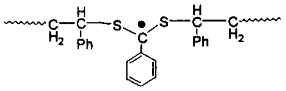
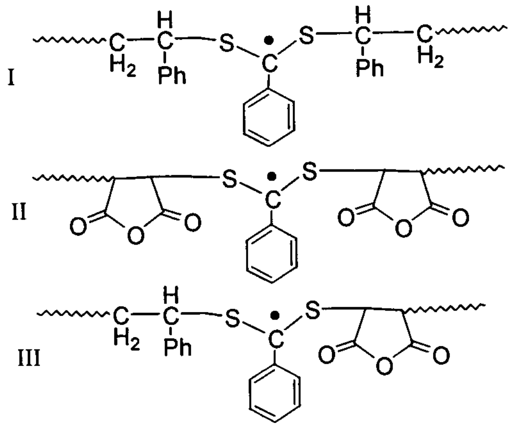
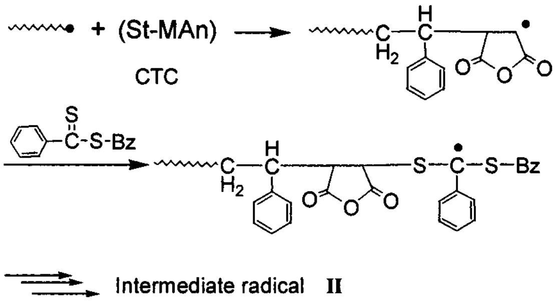
Table 1. ESR Spectral Parameters

radical	hyperfine splittings a_H/G	g-factor	reference
	3.60 (2H, ortho) 1.27 (2H, metha) 4.67 (1H, para) 0.64 (2H, γ-H)	2.0040	This work
	3.67 (2H, ortho) 1.35 (2H, metha) 4.55 (1H, para) 0.49 (2H, γ-H)	2.0041	This work
	3.66 (2H, ortho) 1.41 (2H, metha) 3.96 (1H, para) 0.28 (2H, γ-H)	2.0041	9
		2.0043	9

Scheme 1



Scheme 2



maleic anhydride were first investigated. Both the two systems provided well-resolved and clearly distinct ESR spectra being very similar to those for RAFT polymerization of *n*-butyl acrylate or styrene.[9] The observed ESR spectra for homopolymerizations of styrene along with its simulation are shown in parts a and b of Figure 1, respectively. The observed spectrum was reasonably assigned to be an intermediate radical (**I**) with hyperfine splitting constants (hfc) shown in Table 1. The observed signal is considered to be the same signal as that Hawthorne et al. had measured, but the spectroscopic resolution in the present signal was much higher than the previously observed signal. It means that the values of hfc's can be determined precisely from the present signal. A simulated spectrum could reproduce the observed signal very well by using these hfc values. The ESR spectrum of intermediate radicals in RAFT of maleic anhydride is shown in Figure 1c. It can be seen that this signal is different from the signal of styrene polymerization. The signal showed a so-called line-width alternation due to restricted rotation of C$-$C bonds around the radical center. ESR spectra reported in this research work were measured at 0 °C under irradiation in order to improve the resolution of the spectroscopic lines. At such low temperature, molecular motion would be restricted, and the ESR spectrum showed the line-width alternation. The observed spectrum was reasonably assigned to be an intermediate radical (**II**) with values of hfc's shown in Table 1. Such a spectrum cannot be simulated by the typical isotropic simulation program used as for the case of styrene signal. The simulation spectrum (Figure 1d) was obtained from a specially prepared simulation program in consideration with chemical exchange phenomena.[11] The similarity between parts c and d of Figure 1 can be seen clearly. And finally, the styrene$-$maleic anhydride alternative copolymerization system was investigated by ESR spectroscopy. The observed signal is shown in Figure 1e. Hyperfine splitting values can be determined precisely, especially for protons at the γ-position because the resolution of the present spectrum is much higher than that reported previously.[9] This signal is almost the same

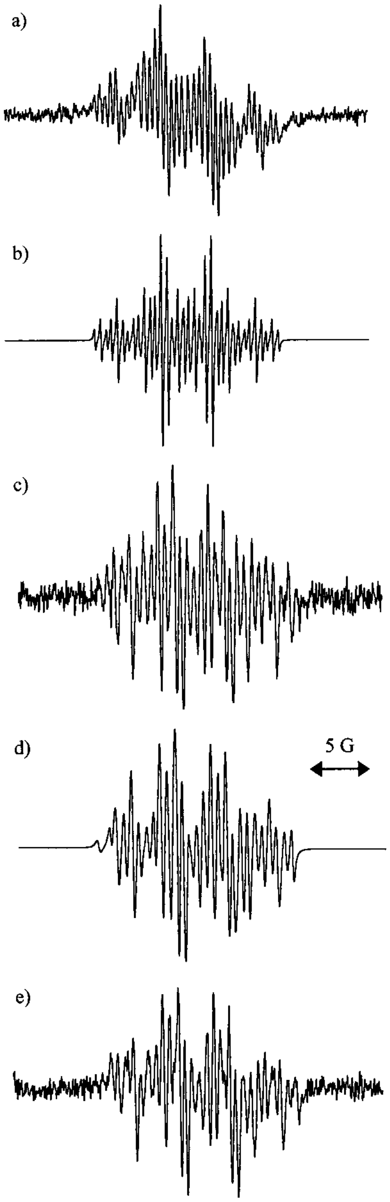


Figure 1. Observed and computer-simulated ESR spectra for the RAFT polymerization of St, MAn, and their copolymerizations in benzene ([St] = [MAn] = 1.0 mol/L, [BTBA] = 0.1 mol/L, [MAIB] = 0.05 mol/L, temperature 0 °C, UV light): (a) observed spectrum for St; (b) simulated spectrum for St; (c) observed spectrum for MAn; (d) simulated spectrum for MAn; (e) observed spectrum for copolymerization of St and MAn.

signal as the case of maleic anhydride homopolymerization system (Figure 1c). A relatively large *g*-factor (2.0040) vs free electron value of 2.0023 shows that there is a significant delocalization of the free spin onto heteroatom sites, i.e., S. At a higher temperature of 35 °C, a weak and poor-resolved signal being similar to that at 0 °C was observed. When the temperature reached 70 °C, there was no observable signal under the present conditions. This is attributed to the greater fragmentation rate of the intermediate radicals and the faster copolymerization rate of MAn and St at higher temperatures. This finding indicates that the intermediate radical during the RAFT copolymerization of MAn and St is **II**, deriving from active MAn-ended propagating radical.

As regards the copolymerization mechanism, if the chain propagation proceeds via the CTC model, there should be only one kind of propagating radical, St-ended or MAn-ended. On the other hand, if the polar transition state model dominates, both radicals should be present during the copolymerization process. Our results are probably indicative of a CTC propagation mechanism for RAFT copolymerization of St and MAn as shown in Scheme 2, at least under conditions of the ESR experiments. It was also reported that the CTC model is viable in a nonpolar and nondonor solvent at a low temperature.[4] However, the polar transition state model cannot be excluded completely because the active propagating radicals were not directly observed by ESR. Further research concerning effects of solvent, temperature, and monomer feed ratio is underway.

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