Macromolecules **1992,** *25,* 3323-3324

Steric Effect of Alkyl Substituents on Propagation Rate Constants of *N*-(2,6-Dialkylphenyl)maleimides in Radical Polymerization

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Received January 26, 1992
Revised Manuscript Received April 10, 1992

Introduction. In previous papers,[1-4] we reported the radical polymerization of N-substituted maleimides bearing various N-substituents and the thermal properties of the resulting polymers. In the studies on polymerization of *N*-(alkyl-substituted phenyl)maleimides (RPhMI),[1] it has been shown that poly(RPhMI)s bearing an alkyl group at the ortho position of the *N*-phenyl ring show excellent thermal stability and superior solubility in many organic solvents including benzene, chloroform, and tetrahydrofuran, while poly(*N*-phenylmaleimide) (poly(PhMI)) is soluble only in polar solvents. Also it was found that the polymerization reactivities, i.e., yields and molecular weights, of the resulting polymers of ortho-substituted RPhMIs decreased with an increase in the bulkiness of the *o*-alkyl groups because of a steric factor of the substituents.

Recently, the kinetics of radical polymerization of dialkyl fumarates,[5-7] dialkyl itaconates,[8,9] and *N*-cyclohexylmaleimide[10] have been investigated by means of electron spin resonance (ESR) spectroscopy on account of the high concentrations of propagating radicals at the steady state. Therefore, we carried out determinations of absolute rate constants of propagation (k_p) in the radical polymerization of RPhMIs with different alkyl substituents (Chart I) by ESR spectroscopy and investigated the steric effects of the substituents on k_p in relation to the reactivities of RPhMIs and their propagating radicals. The preliminary results obtained are reported in this paper.

Experimental Section. RPhMIs were prepared by the method given in the literature.[1,11] Polymerization was performed in a sealed glass tube in the presence of dimethyl 2,2′-azobis(isobutyrate) (MAIB) in benzene at 60 °C. The polymer was precipitated in methanol, and the polymerization rate (R_p) was determined gravimetrically. Radical copolymerization with methyl methacrylate (MMA) was performed similarly. The composition of the copolymers was determined by ^{1}H NMR spectroscopy, and then the monomer reactivity ratios (r_1 and r_2) were calculated by a nonlinear least-squares procedure.[12]

ESR spectra were recorded on a Bruker ESP 300 spectrometer equipped with an X-band (9.48-GHz) microwave unit and 100-kHz field modulation. The measurement parameters are indicated in Figure 1. The radical concentration was determined by a calibration with 1,3,5-triphenylverdazyl from the spectra obtained with a large modulation amplitude (10 G) by accumulation of 10 scans.

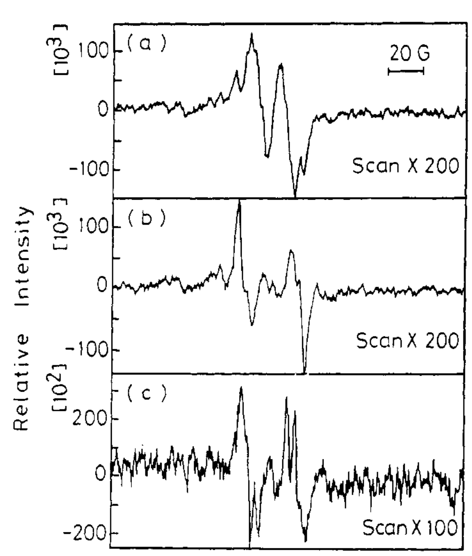
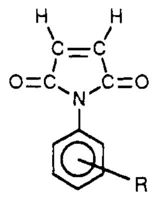


Figure 1. ESR spectra of the propagating radicals of RPhMIs: (a) 2,6-diethyl- and (b) 2,6-dimethyl-disubstituted and (c) 2-methyl-substituted RPhMI. Polymerization conditions: [RPhMI] = 1 mol·L^{-1}, [MAIB] = 5 × 10^{-3} mol·L^{-1} in benzene at 60 °C. Measurement parameters: modulation amplitude, 1.0 G; conversion time, 41 ms; time constant, 164 ms; sweep time, 42 s; power, 10.0 mW; receiver gain, 5 × 10^5; scan number, 200 (a and b) or 100 (c).

Chart I



RPhMI
(R = 2,6-(C_2H_5)$_2$, 2,6-(CH_3)$_2$, 2-CH_3, 4-C_2H_5)

Results and Discussion. Radical polymerization of four RPhMIs ([RPhMI] = 1 mol·L^{-1}) with MAIB ([MAIB] = 5 × 10^{-3} mol·L^{-1}) in benzene at 60 °C was performed. All polymerizations proceeded homogeneously, whereas it was reported that polymerizations of PhMI and its 4-methyl-substituted derivative were accompanied by precipitation of the resulting polymers because of their insolubility in benzene as the solvent.[1] The R_p of RPhMIs bearing 2,6-dialkyl substituents decreased in the order of the steric hindrance of the substituents; i.e., 4-ethyl (11.4 × 10^{-5} mol·L^{-1}·s^{-1}) > 2-methyl (5.15) > 2,6-dimethyl (1.44) > 2,6-diethyl (0.401). It agrees well with our previous results[1] for polymerization initiated with 2,2′-azobis(isobutyronitrile) (AIBN).

The ESR spectra of the propagating radicals were detected under the conditions identical to those of the polymerization above, as depicted in Figure 1. The relative

Table I
Propagation and Cross-Propagation Rate Constants of RPhMIs at 60 °C[a]

				copolymn with MMA (M_1)			
substituent	R_p × 10^5, mol·L^{-1}·s^{-1}	[P•] × 10^6, mol·L^{-1}	k_p, L·mol^{-1}·s^{-1}	r_1	r_2	k_{12},[b] L·mol^{-1}·s^{-1}	k_{21},[b] L·mol^{-1}·s^{-1}
2,6-diethyl	0.401	2.00	2.00	4.78[c]	0.049[c]	76.8	40.8
2,6-dimethyl	1.44	1.06	13.6	3.62[c]	0.070[c]	101	194
2-methyl	5.15	0.277	186	2.22[c]	0.094[c]	165	1980
4-ethyl	11.4 (26.2)[d]	(0.223)[d]	1180	1.69	0.283	217	4170

[a] Polymerization conditions: [RPhMI] = 1 mol·L^{-1}, [MAIB] = 5 × 10^{-3} mol·L^{-1} in benzene. [b] $k_{12} = k_{11}/r_1$, $k_{21} = k_{22}/r_2$, where k_{11} = 367 L·mol^{-1}·s^{-1} reported by Matheson et al.[14] [c] Reference 1. [d] The values in parentheses were determined at [MAIB] = 2 × 10^{-2} mol·L^{-1}.

0024-9297/92/2225-3323$03.00/0
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intensity and shape of the peaks were altered by the substituents. The difference in the hyperfine structures of these spectra seems to be due to the conformational change of the propagating radicals. The conformational structure of the propagating radical is now investigated further.

The intensities of the spectra were in the following order: 2,6-diethyl (2.00×10^{-6} mol·L^{-1}) > 2,6-dimethyl (1.06) > 2-methyl (0.277), where the values in parentheses are the concentrations of the propagating radicals ([P$^{\bullet}$]) determined with a larger modulation amplitude (10 G) by the use of 1,3,5-triphenylverdazyl as a stable radical for calibration. Because the intensity of the spectrum from 4-ethyl-substituted RPhMI was too weak to be estimated precisely, the [P$^{\bullet}$] of the 4-ethyl derivative was determined at a higher initiator concentration ([MAIB] = 2×10^{-2} mol·L^{-1}). The introduction of alkyl groups at the ortho positions increased [P$^{\bullet}$], suggesting that the 2,6-disubstituted RPhMI radicals have a smaller bimolecular termination rate constant due to local steric hindrance around the reacting center and/or the reduced chain flexibility of the polymer.[13] A detailed estimation of k_t will be described elsewhere in the future.

The k_p was calculated by the following relation:

$$k_p = R_p/([\mathrm{P}^{\bullet}][\mathrm{RPhMI}]) \qquad (1)$$

Surprisingly k_p was found to vary from 2 to 1180 L·mol^{-1}·s^{-1} for the 2,6-dimethyl and 4-ethyl derivatives, as shown in Table I, corresponding to the steric bulkiness of the substituents. The decrease in k_p can be due to a decrease in the reactivities of the monomer and the polymer radical because of the introduction of the ortho substituents. Therefore, cross-propagation rate constants were evaluated in radical copolymerization with MMA (M_1). k_{12} and k_{21}, the constants in the following equations, represent the relative reactivities of the RPhMI monomers and the poly(RPhMI) radicals, respectively.

$$\sim\!\sim\mathrm{MMA}^{\bullet} + \mathrm{RPhMI} \xrightarrow{k_{12}} \sim\!\sim\mathrm{RPhMI}^{\bullet} \qquad (2)$$

$$\sim\!\sim\mathrm{RPhMI}^{\bullet} + \mathrm{MMA} \xrightarrow{k_{21}} \sim\!\sim\mathrm{MMA}^{\bullet} \qquad (3)$$

k_{12} and k_{21} can be calculated as $k_{12} = k_{11}/r_1$ and $k_{21} = k_{22}/r_2$, respectively. The monomer reactivity ratios for 2-substituted and 2,6-disubstituted RPhMIs have already been determined in the previous work.[1] For the calculation of k_{12}, the reported k_p value of MMA (367 L·mol^{-1}·s^{-1})[14] was used as k_{11}.

The k_{12} values changed from 76.8 to 217 L·mol^{-1}·s^{-1}, and the k_{21} values were from 40.8 to 4170 L·mol^{-1}·s^{-1}, depending on the substituents, as summarized in Table I. These results indicate that the decrease in the reactivities of both the monomer and the polymer radical leads to the decrease in k_p, i.e., k_p of 4-ethyl-substituted RPhMI (1180 L·mol^{-1}·s^{-1}) is 600-fold as large as k_p of the 2,6-diethyl derivative (2 L·mol^{-1}·s^{-1}). Moreover, the k_{21} of the 4-ethyl derivative are 100-fold larger than that of the 2,6-diethyl one, while the change of k_{12} was relatively small (3-fold), indicating that the decreasing reactivity of the polymer radical is more significant. More detailed experimental results and discussions will be published elsewhere.

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