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Reactivity of Uncyclized Diene Radical in the Cyclocopolymerization of Diallyl Ether with Maleic Anhydride

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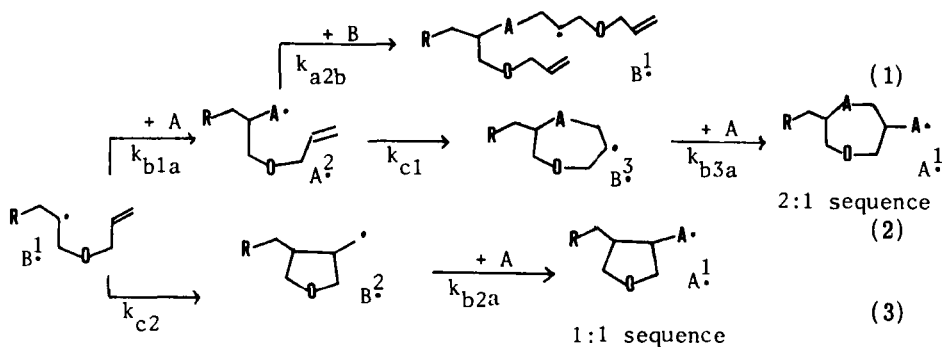
ABSTRACT

The initial rate of the radical copolymerization of diallyl ether (DAE) with maleic anhydride (MA) in benzene and acetone, that produced a soluble copolymer of composition between 1:1 and 2:1, was maximum between 1:1 and 2:1 feed composition in MA. The rate decreased gradually as the polarity of the solvent increased. The ratio (r_b) of the rate constants of intermolecular cross-propagation of uncyclized DAE radical and of the intramolecular homocyclization was 0.53 ± 0.10 in acetone and $0.42 \pm 0.10 \text{ dm}^3/\text{mol}$ in benzene. There was no detectable temperature dependency of the ratio between 30 and 60°C, indicating that the activation energy difference between the two reactions of the uncyclized DAE radical was negligible.

INTRODUCTION

Polar monomers such as sulfur dioxide (SO₂) and maleic anhydride (MA) were found to cyclocopolymerize with 1,6-dienes such as diallyl ether (DAE) by a radical mechanism [1, 2]. Since the monomers did not readily homopolymerize in ordinary conditions, a cyclocopolymer-

zation scheme based on cross-propagation and the cyclization of the 1,6-diene unit, that lead to 1:1 and 2:1 sequences, was proposed in order to explain the fact that the copolymers had a copolymer composition between 1:1 and 2:1 in the monoolefin unit in a wide range of feed monomer compositions.



The copolymer composition equation based on this scheme [3] enables the evaluation of ratios of the rate constants of the intermolecular cross-propagation and intramolecular cyclization. In the cyclocopolymerization of 1,6-dienes, which was first proposed by Butler and Angelo [4], there is a considerable degree of interest as to the reactivity of the uncyclized diene radical in undergoing the intramolecular cyclization. The composition study of the cyclocopolymerization would provide quantitative information on the relative reactivity of the uncyclized diene radical.

In this article the cyclocopolymerization of DAE with MA is studied in benzene and acetone at various temperatures.

RESULTS AND DISCUSSION

Initial Rate of Copolymerization

The time-conversion curves in Fig. 1 show that the initial rate is constant up to about 10% conversion. The gravimetrically measured initial rate of copolymerization is shown in Fig. 2 with respect to the composition of the feed monomer mixture. The rate was maximum between 1:1 and 2:1 feed composition in MA, reflecting the overall composition of the copolymer produced, the rate maximum being closer to 1:1 feed composition in less polar benzene. This may suggest the importance of a polar effect in the cross-propagation of this copolymerization. The overall energy of activation was determined by the Arrhenius plot at each feed composition (Table 1). Good straight-line

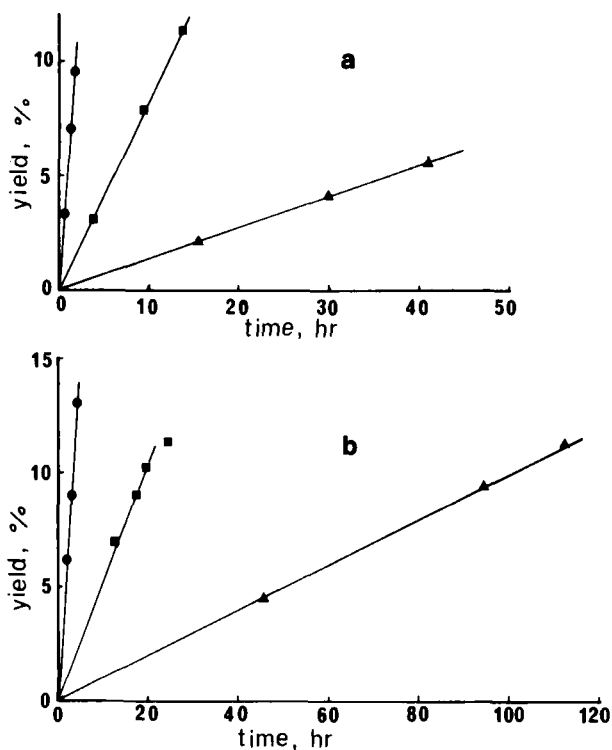


FIG. 1. Time-conversion curves in benzene (a) and in acetone (b). Mole fraction of MA in feed monomer mixture, $f_{MA} = 0.50$. $[DAE + MA] = 1.68 \text{ M}$, $[AIBN] = 3.25 \times 10^{-2} \text{ M}$ (in benzene) or $6.91 \times 10^{-2} \text{ M}$ (in acetone). (●) At 60°C , (■) at 45°C , (▲) at 30°C .

plots were obtained in all cases to give average activation energies of 94 and 97 kJ/mol in benzene and acetone, respectively. It is interesting to note that the overall activation energy is generally a little larger in acetone and that it seems to show a minimum, the value being larger when the concentration of MA in the feed is dominant. These may imply that a polar interaction between the oppositely polarized radical and the monomer at the transition state is important and that the addition of MA requires a large activation energy.

The initial rate, reflecting the polar effect, was slower in more polar acetone (dielectric constant $\epsilon = 20.70$ at 25°C [5]) than in benzene ($\epsilon = 2.284$ at 20°C [5]). Although every solvent exerts its specific solvent effect, the effect of solvent polarity on the initial rate is apparent in Fig. 3. The initial rate decreases gradually with an increase of solvent polarity. On the other hand, it is reported that the rate decreases

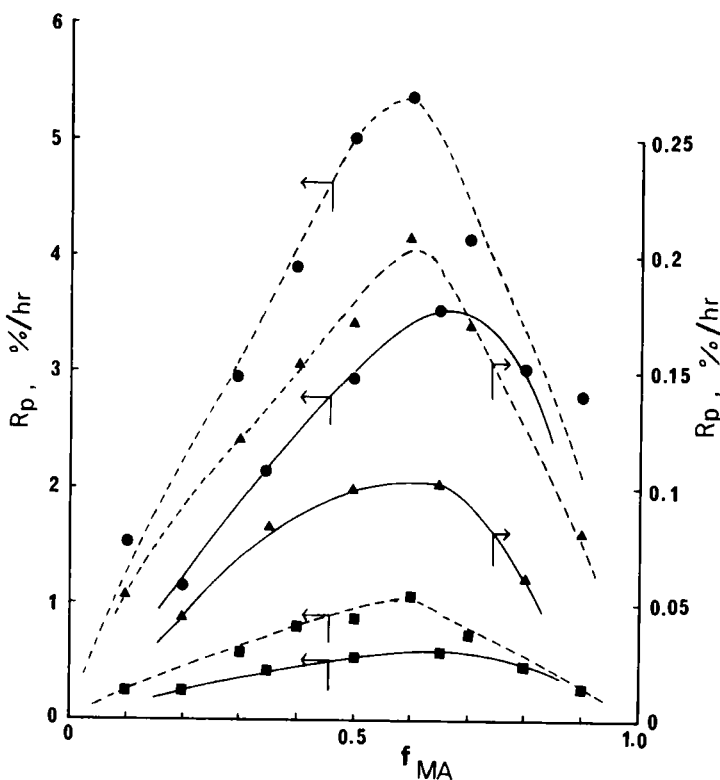


FIG. 2. Initial rate of copolymerization (R_p) with respect to the mole fraction of MA in feed monomer mixture (f_{MA}). The solid lines are the rates measured in acetone and the broken lines are the rates in benzene. $[DAE + MA] = 1.68 \text{ M}$, $[AIBN] = 6.91 \times 10^{-2} \text{ M}$ (in acetone) or $3.25 \times 10^{-2} \text{ M}$ (in benzene). (●) At 60°C , (■) at 45°C , (▲) at 30°C .

much more sharply when a charge-transfer complexation participates in a copolymerization due to the rapid decrease of the equilibrium constant of the complexation with solvent polarity, the rate-solvent polarity curve concaving upward [6]. Participation of the charge-transfer complex of the comonomers was ruled out because it was not possible to detect complexation in UV and PMR measurements in CCl_4 . It is considered that the polar interaction at the transition state of cross-propagation is the major factor that enables this copolymerization to proceed by lowering the activation energy.

TABLE 1. Overall Energy of Activation, E_a

In benzene		In acetone	
Mole fraction of MA in feed	E_a (kJ/mol)	Mole fraction of MA in feed	E_a (kJ/mol)
0.10	95.1	0.20	91.5
0.30	94.2	0.35	90.6
0.40	89.2	0.50	94.5
0.50	92.6	0.65	99.2
0.60	90.1	0.80	108.6
0.70	93.1	Average	96.9
0.90	105.3		
Average	94.2		

Copolymer Composition

The copolymer composition determined from the titration of the MA unit is shown in Figs. 4 and 5. The composition was between 1:1 and 2:1 in MA units in a wide range of feed monomer composition. The copolymer composition equation based on the cross-propagation and the intramolecular homocyclization of DAE (Eqs. 1, 2, and 3) is [3]:

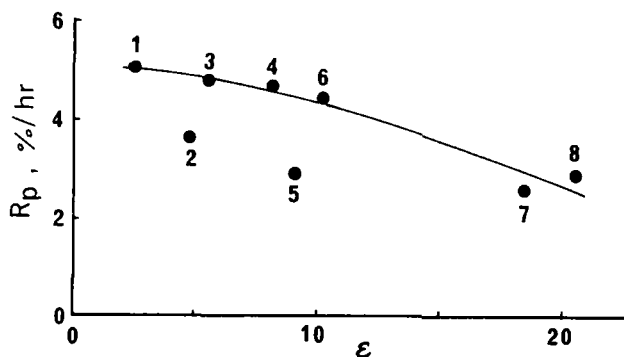


FIG. 3. Initial rate of copolymerization at 60°C (R_p) versus the dielectric constant of solvents (ϵ). $[DAE + MA] = 1.68 \text{ M}$, $[DAE]/[MA] = 1$. Solvents: 1, benzene; 2, CHCl_3 ; 3, chlorobenzene; 4, $\text{CHCl}_2\text{CHCl}_2$; 5, CH_2Cl_2 ; 6, $\text{CH}_2\text{ClCH}_2\text{Cl}$; 7, butanone; 8, acetone.

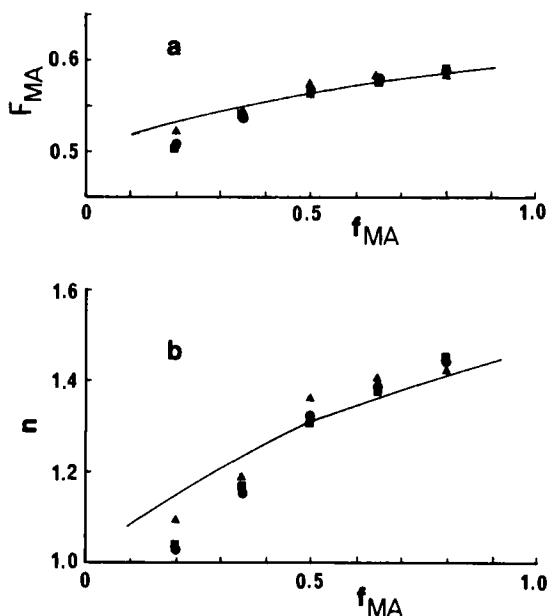


FIG. 4. Copolymer composition curves in acetone. (a) The mole fraction of MA in copolymer (F_{MA}) versus the mole fraction of MA in the feed monomer mixture (f_{MA}). (b) The mole ratio of MA to DAE in copolymer (n) versus f_{MA} . (•) At 60°C, (■) at 45°C, (▲) at 30°C. The solid lines are calculated by using $r_b = 0.53 \text{ dm}^3/\text{mol}$. $[\text{DAE} + \text{MA}] = 1.68 \text{ M}$, $[\text{AIBN}] = 6.91 \times 10^{-2} \text{ M}$.

$$n = \frac{-d[A]/dt}{-d[B]/dt} = \frac{(r_b[B] + 1)([A] + 1/r_b) + [A]}{(r_b[B] + 1)([A] + 1/r_b)} \quad (4)$$

where n is the mole ratio of MA unit to DAE unit in the copolymer, and $[A]$ and $[B]$ are the molar concentrations of the monoolefin (MA) and the diene (DAE). $r_a = k_{a2b}/k_{c1}$ is the ratio of the rate constants for the radical A^2 in undergoing cross-propagation with the diene and in undergoing intramolecular cyclization to give a cyclic radical B^3 . $r_b = k_{b1a}/k_{c2}$ is the ratio of the rate constants for the uncyclized diene radical B^1 in undergoing cross-propagation with the monoolefin and in undergoing intramolecular homocyclization to give radical B^2 .

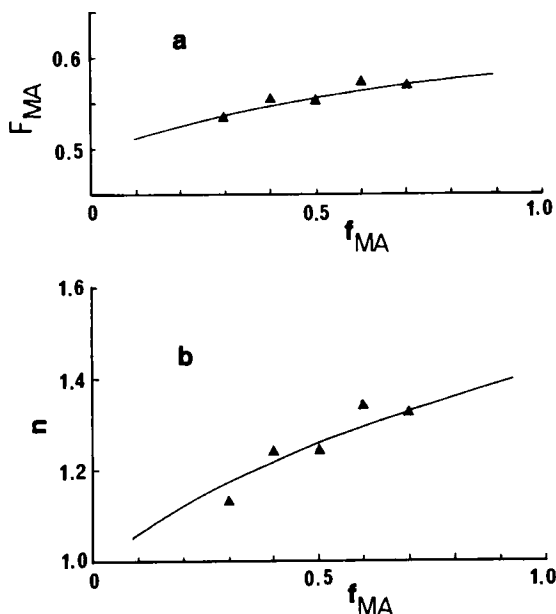


FIG. 5. Copolymer composition curves in benzene at 30°C. (a) The mole fraction of MA in copolymer (F_{MA}) versus the mole fraction of MA in the feed monomer mixture (f_{MA}). (b) The mole ratio of MA to DAE in copolymer (n) versus f_{MA} . The solid lines are calculated by using $r_b = 0.42 \text{ dm}^3/\text{mol}$. $[\text{DAE} + \text{MA}] = [\text{AIBN}] = 3.25 \times 10^{-2} \text{ M}$.

Since the copolymers, which were soluble in polar solvents, did not show residual C=C double bonds in IR and PMR, it was considered that the cyclization of the radical A^2 was complete, being benefited by the opposite polarity and the proximity of the reactants, and $r_a \approx 0$. The simplified equation (5) was used to evaluate r_b values:

$$n = \frac{([A] + 1/r_b) + [A]}{[A] + 1/r_b} \quad (5)$$

The copolymer composition did not change significantly with temperature. The ratio r_b was $0.53 \pm 0.10 \text{ dm}^3/\text{mol}$ in acetone between 30 and 60°C and it was $0.42 \pm 0.10 \text{ dm}^3/\text{mol}$ in benzene at 30°C. The

r_b value in benzene at 60°C, calculated by reported data [3], was also 0.4 dm³/mol. The indiscernible change in r_b with temperature corresponds to a negligible activation energy difference between the intramolecular homocyclization of DAE radical B¹ and its cross-propagation with MA, i.e., $E_a(k_{c2}) - E_a(k_{b1a}) \approx 0$. It is interesting to note that in the cyclocopolymerization of DAE with SO₂ in acetone, the activation energy was larger in cross-propagation with SO₂ than intramolecular homocyclization of the DAE radical by 40 kJ/mol [7]. It is considered that the polar interaction may be more effective with the strongly polarized MA monomer at the transition state and that extra energy may be needed to rehybridize the orbitals of the sulfur atom when SO₂ reacts with a radical. It appears remarkable that the intramolecular homocyclization of the allyl group has only a comparable activation energy with that for the cross-propagation which is assisted by polar interaction. Butler [8] has proposed the formation of an interspatial nonclassical radical at the transition state of the intramolecular cyclization of 1,6-dienes that would lower the activation energy. On the other hand, the rate constant of the homocyclization of the DAE radical is always about twice as large in magnitude as that of the cross-propagation with MA, although the intermolecular cross-propagation is more favorable thermodynamically due to the larger decrease in entropy. This may be consistent with the kinetic formation of five-membered rings by 1,6-dienes in cyclopolymerization [9] and cyclocopolymerization [7, 10].

EXPERIMENTAL

Reagent grade DAE (Tokyo Kasei) and solvents were fractionally distilled before use. Diethyl ether was dried over sodium wire. Reagent grade MA (British Drug House) and 2,2'-azobisisobutyronitrile (AIBN) (T.K.) were recrystallized from dry benzene and methanol, respectively.

Polymerization was carried out in glass ampules of 25-40 cm³ capacity which were sealed after degassing of the system by the freeze-thaw method under high vacuum. The ampules were immersed in an oil-bath whose temperature was controlled to $\pm 0.1^\circ\text{C}$. The polymer was separated and purified by precipitating it in diethyl ether from acetone solution. IR (KBr pellet): 1860(s) and 1770(s) cm⁻¹ (five-membered anhydride), 1080(m) cm⁻¹ (ether C-O-C). PMR (in acetone-d₆ at 30°C, all broad peaks: 1.11 δ (-CH₂-), 1.73 δ (tertiary C-H), 2.70 δ (tertiary C-H of MA unit), 3.50-3.90 δ (-CH₂-O-CH₂-).

The content of MA unit in the copolymer was determined by back-titrating about 100 mg of the copolymer conductometrically with 0.05 M NaOH and 0.05 M HCl. Philips PR9500 was used.

Perkin-Elmer Type 597 IR spectrophotometer, Varian Type 100 60 MHz PMR spectrophotometer, and Unicam SP8-100 UV/visible spectrophotometer were used.

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