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RADICAL POLYMERIZATION OF METHACRYLIC ISOBUTYRIC ANHYDRIDES: MUCH LOWERED CEILING TEMPERATURE COMPARED TO METHACRYLATES

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ABSTRACT

In a previous article in connection with the mechanistic discussion of radical cyclopolymerization of nonconjugated dienes, the ceiling temperature of methacrylic isobutyric anhydride (MIBA) as a monoene counterpart of methacrylic anhydride was expected to be much lower compared to methacrylates. The radical polymerization behavior of MIBA is discussed in detail in terms of the dependence of the rate of polymerization (R_p) on monomer concentration, polymerization temperature, and solvent polarity compared to methyl methacrylate. The increased significance of unimolecular depropagation in contrast to bimolecular propagation was clearly demonstrated with decreased monomer concentration, higher polymerization temperature, and increased solvent polarity as reflected in a reduced rate of polymerization compared to an ordinary vinyl polymerization, suggesting the much lowered ceiling temperature of MIBA compared to methacrylates.

INTRODUCTION

In a previous article [1] it was suggested that, in the cyclopolymerization of nonconjugated dienes, intramolecular head-to-head addition of the uncyclized radical to the internal double bond would be promoted under specific polymerization conditions, i.e., above the ceiling temperature for head-to-tail propagation ($\Delta G_{ht} \geqslant 0$) in the polymerization of the corresponding monoene counterparts. In this connection, five-membered ring formation via intramolecular head-to-head addition has been explored in the cyclopolymerization of methacrylic anhydride (MA) [2]. This study was considered to be significant because the ceiling temperatures in the polymerization of methacrylates, as typical α,α-disubstituted ethylenes, are quite low [3] compared to those of ordinary monosubstituted ethylenes. Moreover, the ceiling temperature of methacrylic isobutyric anhydride (MIBA) as the monoene counterpart of MA is expected to be much lower than that of methacrylates from our proposed mechanism based on polymerization equilibrium for the cyclopolymerization of acrylic anhydride [4]. The lower ceiling temperature should arise from the electrostatic repulsion between polar anhydride units, and this electrostatic repulsion would be enhanced in polar media.

In radical polymerization accompanied by termination via reaction between growing radicals, it is difficult to determine the exact ceiling temperature for a head-to-tail propagation. However, near the ceiling temperature, the depropagation reaction equilibrated with propagation should be significant for the reaction of a growing radical. That is, the polymerization would not obey the usual radical vinyl polymerization behavior under specified conditions near the ceiling temperature. Thus, the radical polymerization of MIBA was examined in detail, and the increased significance of depropagation with increased polymerization temperature, decreased monomer concentration, and increased solvent polarity was established, suggesting a much lowered ceiling temperature of MIBA compared to methacrylates.

EXPERIMENTAL

MIBA monomer was prepared by the reaction of methacrylyl chloride with isobutyric acid according to the synthetic method for acrylic propionic anhydride [5]. The crude product was vacuum-distilled, and the middle fraction was collected: bp 64-65°C/4 torr, n_D^{20} = 1.4324. MA monomer was prepared as described previously [6].

Isobutyric anhydride (IBA), methyl methacrylate (MMA), azobisisobutyronitrile (AIBN), as the initiator, benzene, dioxane, cyclohexanone, benzonitrile, γ-butyrlactone, and acetonitrile, as solvents, were commercially available reagents and purified by conventional methods.

Polymerization was carried out in ampules. After a given reaction time, the reaction mixture was poured into a large volume of hexane to precipitate the polymer, which was successively reprecipitated in the acetone-hexane system, dried under reduced pressure, and subjected to analysis. The analyses of the polymer obtained were conducted as described previously [4, 6].

RESULTS AND DISCUSSION

Preparation of MIBA Monomer

In an earlier paper [7] the syntheses of several unsymmetrical acrylic anhydrides, including acrylic propionic anhydride, MIBA, dimethacrylic fumaric anhydride, methacrylic benzoic anhydride, and methacrylic cinnamic anhydride, were attempted, but without success. The disproportionated, symmetrical product, or a mixture of it and the desired product were obtained in all cases. For example, acrylic propionic anhydride was obtained only as the monomer which contained some disproportionated propionic anhydride as impurity.

Later, on consideration of the enhanced rate of cyclopolymerization of divinyl monomers over that of the corresponding monovinyl monomers, Butler and Kimura [8] tried to prepare MIBA as the monovinyl monomer to compare with MA, but its inherent instability precluded its isolation in a pure state. In both cases the metathesis of an acyl halide and an alkali metal carboxylate was employed.

In this work the method of Brotherton, Smith, and Lynn [9] for the preparation of acrylic and methacrylic anhydrides was modified to obtain MIBA monomer. Thus, isobutyric acid was treated with methacrylyl chloride in the presence of triethylamine. The refractive index, n_D^{20}, was measured as 1.4324; this value is somewhat higher than the mean value (1.4292) of MA (1.4535) and IBA (1.4049) (the n_D^{24} value of 1.4235 which had been reported earlier [8] appeared to be for a mixture of two or three anhydrides).

The ^{1}H and ^{13}C NMR and IR spectra of this monomer were then compared with those of MA-IBA (1:1 molar) mixture. As was the case for acrylic propionic anhydride [5], no significant difference was observed in the ^{13}C NMR spectra. However, we can conclude that the MIBA monomer prepared by us is almost pure by considering the following facts in addition to the refractive index and the narrow boiling point range. Figure 1 shows the ^{1}H NMR spectra of MIBA and an equimolar MA-IBA mixture. The area of each peak corresponded exactly to the number of the assigned protons. Peak splittings of both spectra were the same, in contrast to the case in which acrylic propionic anhydride gave peak splittings different from those of the equimolar acrylic anhydride-propionic anhydride mixture [5]. However, a precise comparison of both spectra demonstrated a clear difference in chemical shifts of the vinyl methylene and α-methyl protons of the methacrylic moiety and the methyne proton of the isobutyric moiety. So we measured the ^{1}H NMR spectrum of a mixture of MIBA and equimolar MA-IBA mixture, in which both peaks assigned to MIBA and equimolar MA-IBA mixture, respectively, were clearly detected, supporting high purity of the MIBA monomer.

Accordingly, the spectrum of MIBA was distinguishably different from that of an equimolar mixture of MA and IBA, as shown in Table 1.

Earlier, contamination of MIBA was postulated to arise from the disproportionation reaction of MIBA to give MA and IBA [7]. In this connection the disproportionation reaction of acrylic propionic anhydride was experimentally examined and clearly detected in a previous article [5]. Accordingly, both solutions of MIBA and an equimolar MA-IBA mixture in acetonitrile were heat treated as described previously [5], but no disproportionation reaction was observed.

TABLE 1. IR Absorptions Characteristic of Carbonyl Groups of Carboxylic Anhydrides

Anhydride	$\nu_{C=O}$, cm^{-1}
MIBA	1 800, 1 725
MA	1 782, 1 720
IBA	1 810, 1 740
MA-IBA[a]	1 809, 1 783, 1 740, 1 722

[a] Equimolar mixture.

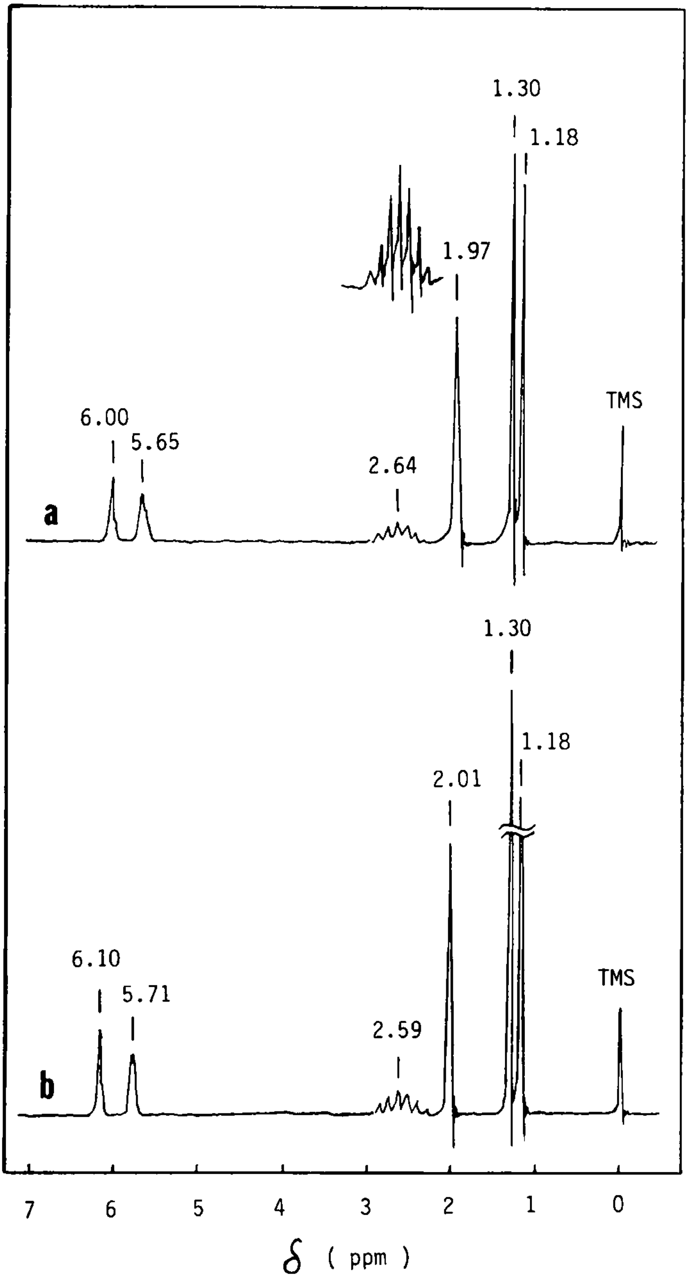

FIG. 1. ^{1}H NMR spectra of (a) MIBA and (b) equimolar MA-IBA mixture in CCl_4.

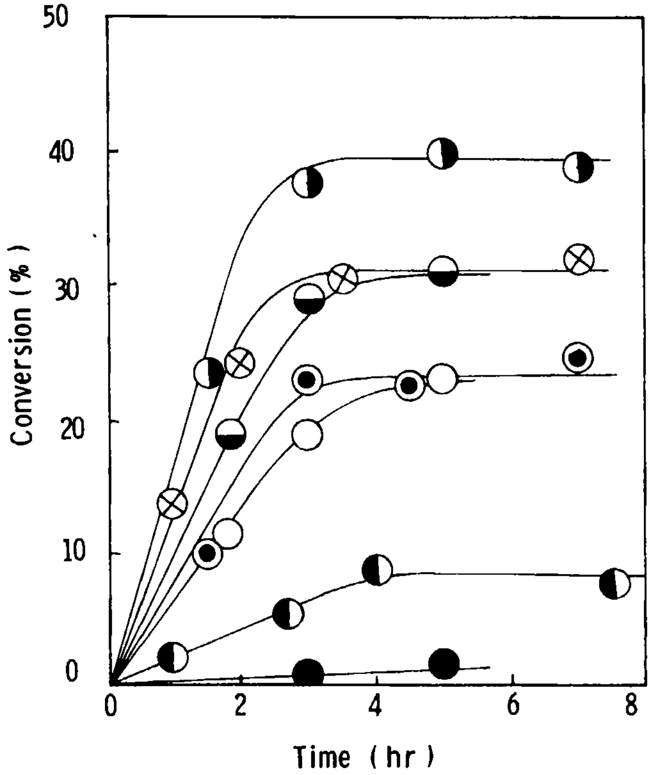

FIG. 2. Time-conversion curves in solution polymerization of MIBA in benzonitrile at 60°C. AIBN (mol/L) dilution ratio: (◑) 0.1, 1/8; (⊗) 0.1, 1/16; (◒) 0.05, 1/16; (◉) 0.1, 1/32; (○) 0.05, 1/32; (◐) 0.1, 1/64; (●) 0.1, 1/128.

Dependence of Rate of Polymerization on Monomer Concentration

Under polymerization conditions where depropagation equilibrated with propagation would be significant for the reaction of a growing radical, an abnormal polymerization behavior would be observable compared to an ordinary vinyl polymerization.

Figure 2 shows the time-conversion curves in solution polymerizations of MIBA in benzonitrile at various AIBN concentrations and dilution ratios. In all cases, polymerizations leveled off at definite conversions which were quite

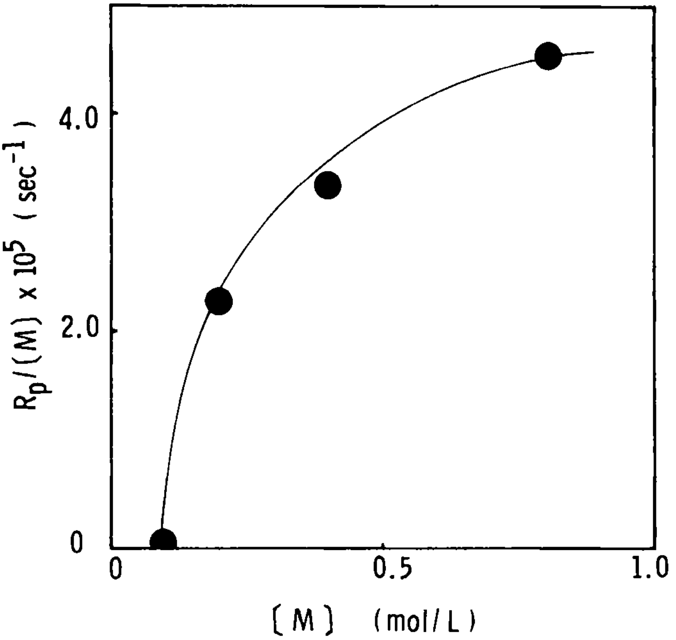

FIG. 3. Relationship between $R_p/[M]$ and [M] in solution polymerization of MIBA in benzonitrile with 0.1 mol/L of AIBN at 60°C.

reduced on dilution but independent of initiator concentration, suggesting an equilibrated polymerization. The unimolecular depropagation in contrast to bimolecular propagation should be significant on dilution. For this reason the dependence of the rate of polymerization R_p on monomer concentration was examined in detail.

Figure 3 shows the relationship between $R_p/[M]$ and [M]. R_p was estimated from the initial slopes of time-conversion curves at an early stage of polymerization. The usual first-order dependency of R_p on monomer concentration for a radical vinyl polymerization was not observed. As expected, deviation from first-order dependence was accelerated clearly on dilution, suggesting increased significance of depropagation with decreasing monomer concentration.

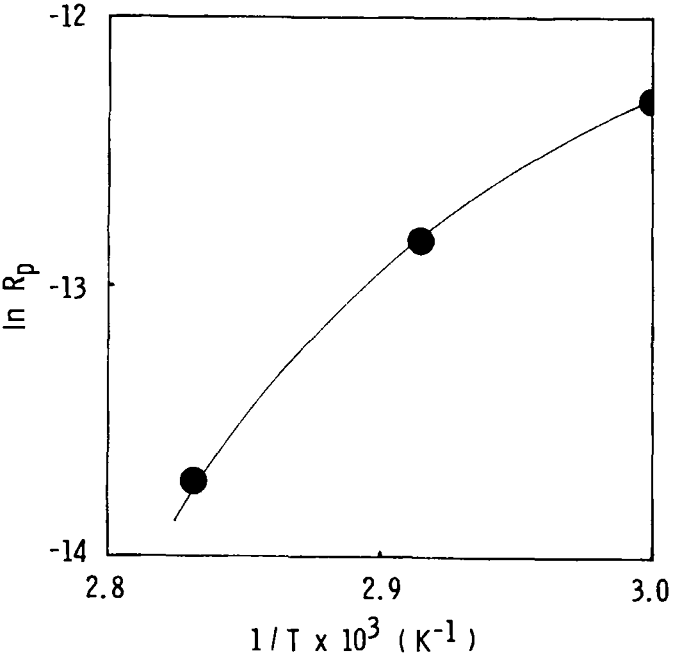

FIG. 4. Plot of ln R_p vs $1/T$ in solution polymerization of MIBA in benzonitrile with 0.1 mol/L of AIBN at a dilution ratio of 1/32 and 60, 70, and 80°C.

Dependence of Rate of Polymerization on Temperature

At a monomer concentration in which deviation from first-order dependence of R_p on monomer concentration was considerable, as shown in Fig. 3, the dependence of R_p on polymerization temperature was examined in detail.

As shown in Fig. 4, R_p decreased with increasing temperature in a manner completely opposite to the usual vinyl polymerization behavior. This is in line with increased significance of depropagation at the elevated temperature.

Dependence of Rate of Polymerization on Solvent Polarity

As mentioned in the Introduction, depropagation is expected to be induced by the electrostatic repulsion between the polar anhydride units. In this con-

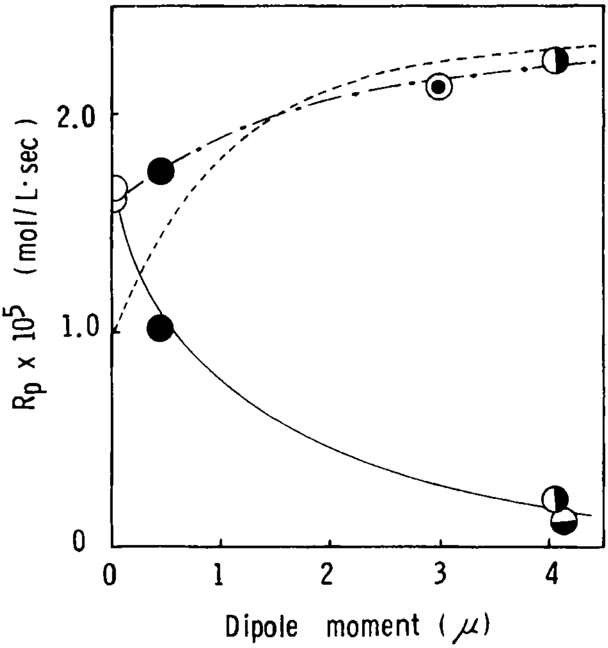

FIG. 5. Relationship between R_p and solvent dipole moment in solution polymerization of MIBA and MMA in (○) benzene, (●) dioxane, (◉) cyclohexanone, (◑) benzonitrile, and (◒) γ-butyrolactone with 0.1 mol/L of AIBN. Monomer, monomer concentration (mol/L), temperature (°C): (-··-) MIBA, 0.8, 50; (—) MIBA, 0.2, 70; (– –) MMA, 0.2, 70.

nection, depropagation would become increasingly significant with increasing solvent polarity because the polarization of carbonyl groups of anhydride units would be enhanced in polar media.

Figure 5 shows the dependence of R_p on solvent polarity, along with the polymerization results of MMA for comparison. As mentioned above, depropagation is not significant at a high monomer concentration and at a low polymerization temperature. Thus, the results obtained at a monomer concentration of 0.8 mol/L and 50°C were in accordance with those of MMA, the ceiling temperature of which is much higher (for example, 164°C in bulk) [10]. However, at 0.2 mol/L of monomer concentration and 70°C, where the significance of depropagation is easily expected from Figs. 3 and 4, R_p was reduced by an increase in the solvent polarity. This suggests increased significance of depropagation in polar media.

Here it should be noted that the latter polymerization conditions of MIBA were the same as in the comparable cases of MMA. Comparison of both results clearly demonstrates that the ceiling temperature of MIBA is much lowered compared to MMA.

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