Solvent and Temperature Effects in the Radiation-Initiated Synthesis of Stereoregular Poly(methacrylic acid)[1a]

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ABSTRACT: Poly(methacrylic acid) was synthesized from the monomer in methanol, 1-propanol, and 2-propanol solvents over a temperature range of −115 to +97° using cobalt 60 γ radiation as the initiator. The triad fractions of the polymers were determined from 60-MHz proton resonance spectra. The syndiotacticity of the polymers increased with decreasing polymerization temperature in all three solvents. At a given temperature, the fraction of *rr* triads increased in the same order as the bulkiness of the alcohol solvent. This solvent effect was related to the hydrogen bonding of the solvent to monomer and to acid groups in the polymer.

In a 40-MHz proton magnetic resonance analysis of poly(methyl methacrylate) (PMMA), Bovey and Tiers showed that the three α-methyl proton peaks are characteristic of stereoregular triad structures.[2] If the dyad placements are designated *m* for *meso* (isotactic) and *r* for racemic (syndiotactic), then the three possible triad structures are *mm*, *mr* (= *rm*), and *rr* (formerly called isotactic, heterotactic, and syndiotactic triads, respectively). In a study of the free-radical addition polymerization of methyl methacrylate, Bovey[3] observed that the addition was predominantly racemic and the fraction of *rr* triads increased with decreasing polymerization temperature. This temperature dependence of the stereoregularity can be explained by assuming that differences exist in the enthalpy of activation for racemic and *meso* addition. From transition state theory, Bovey attributed the tendency toward increasing syndiotacticity to a small additional activation enthalpy (about 775 cal) necessary for *meso* addition. Otsu repeated Bovey's work and obtained a slightly different value for the activation enthalpy difference and a nonzero activation entropy difference.[4] Fox and Schnecko observed that the stereospecificity of PMMA prepared by free-radical addition is unaffected by polymerization variables such as the conversion, the initiator, and the presence of a wide variety of solvents.[5]

We have prepared poly(methacrylic acid) (PMAA) by cobalt 60 γ-radiation initiated polymerization in methanol, 1-propanol, and 2-propanol solvents. Unlike methyl methacrylate, the polymerization of the highly polar monomeric acid in polar solvents might be expected to produce polymers whose stereosequencing is sensitive to the molecular structure of the solvent.

Experimental Section

Solutions of distilled methacrylic acid monomer in dry (less than 0.005% water) methanol, 1-propanol, and 2-propanol were sealed under vacuum in glass vials. The samples were polymerized in the liquid state at constant temperature by irradiating them with a 10-Mrad dose of cobalt 60 γ-radiation. An Atomic Energy of Canada Gammacell 200 source providing a dose rate of 0.40 Mrad/hr was utilized. After irradiation, the polymer solutions in methanol were clear, while the polymer solutions in 1-propanol and 2-propanol were opaque and extremely viscous; all solutions were visually homogeneous. The polymers were precipitated by addition of a solution of benzene (about 10 vol %) and hexane, and subsequently dried under vacuum at 50°. Conversions fell in the range of 30–60%.

The PMAA samples were esterified with diazomethane using the technique of Katchalsky and Eisenberg.[6] Possible traces of polyethylene[7] were removed by filtering a chloroform solution of the methylated polymer through sintered glass. Solutions (15% by weight) of the esterified polymers in chloroform were prepared for nmr analysis. The 60-MHz proton resonance spectra were obtained at 90° with a Varian A60 spectrometer. The fractions of triads in the polymers were determined from the α-methyl proton region using the method of Bovey.[2] The triad fractions reported are the average of the fractions obtained from at least two samples prepared under identical conditions. In all sets of samples, the individual *rr* and *mr* (=*rm*) triad fractions fluctuated about ±0.5% (absolute) about the same value; the fluctuation of the mm triad fractions was about ±1%. Viscosity average molecular weights of the polymers were in the range of 40,000–80,000.

Results and Discussion

The fractions of triads in the polymers are summarized in Table I. In a given solvent, the syndiotacticity increases as the polymerization temperature decreases. At a given temperature, the syndiotacticity increases in the same order as the bulkiness of the alcohol solvent. In 1-propanol solvent, the fraction of *rr* triads at a given temperature is slightly larger in the more dilute solution.

All nmr spectra utilized in this study were obtained with a 60-MHz instrument. Ideally, a higher field instrument is desired so that more precise information of the stereosequence distributions can be obtained. The present data, however, are sufficiently accurate to establish that differences in stereosequencing do indeed

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[1] (a) Presented at the 158th Meeting of the American Chemical Society, New York, N. Y., Sept 1969; (b) to whom correspondence should be addressed; (c) submitted in partial fulfillment of the requirements for the degree of Master of Science.

[2] F. A. Bovey and G. V. D. Tiers, *J. Polym. Sci.*, **44**, 173 (1960).

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TABLE I
STEREOREGULARITY OF PMAA

Solvent	MAA, vol %	Temp, °C	$P \times 100^a$ rr ±0.5	 rm ±0.5	 mm ±1.0
Methanol	20	95	64.5	34.4	1.1
		42	71.7	26.7	1.6
		0	75.0	24.6	0.4
		−78	83.8	16.2	0
2-Propanol	20	69	70.9	26.7	2.4
		0	77.4	21.5	1.1
		−40	88.4	11.2	0.4
		−78	95.0	5.0	0
1-Propanol	20	80	67.7	30.3	2.0
		42	72.0	26.2	1.8
		0	71.8	26.4	1.8
		−78	87.1	12.0	0.9
		−115	92.0	8.0	0
1-Propanol	10	80	69.5	27.6	2.9
		42	74.8	23.1	2.1
		0	75.5	23.1	1.4
		−78	88.0	12.0	0

[a] P values are the average triad fractions of at least two samples.

TABLE II

Solvent	MAA, vol %	$\Delta(\Delta H_p^{\ddagger})$, cal	$\Delta(\Delta S_p^{\ddagger})$, eu
Methanol	20	800 ± 100	−0.4 ± 0.2
1-Propanol	10	1090	−0.1
1-Propanol	20	930	−0.25
2-Propanol	20	1750	+1.7

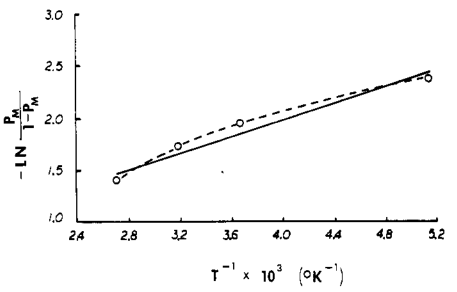

Figure 1. The dependence of P_m on temperature for the polymerization of 20% methacrylic acid in methanol.

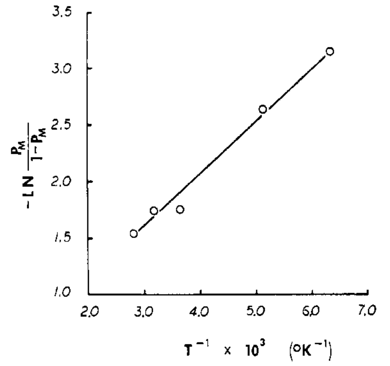

Figure 2. The dependence of P_m on temperature for the polymerization of 20% methacrylic acid in 1-propanol.

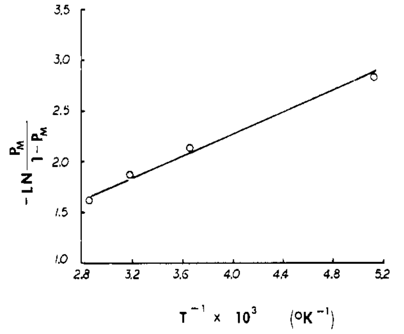

Figure 3. The dependence of P_m on temperature for the polymerization of 10% methacrylic acid in 1-propanol.

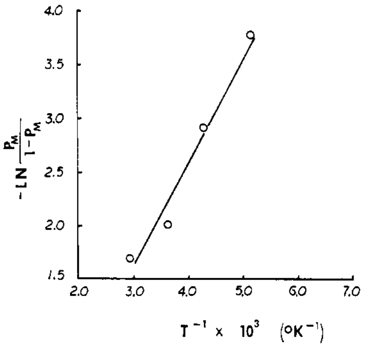

Figure 4. The dependence of P_m on temperature for polymerization of 20% methacrylic acid in 2-propanol.

exist among samples and that these differences are related to various polymerization conditions.

Bovey[3] has reported that the difference in the activation enthalpy of the syndiotactic and isotactic addition processes for Bernoullian polymerization is

$$\Delta(\Delta H_p^{\ddagger}) = \Delta H_m^{\ddagger} - \Delta H_r^{\ddagger} = -R\frac{\partial \ln [P_m/(1 - P_m)]}{\partial(1/T)} \tag{1}$$

where $\Delta H_m^{\ddagger}$ and $\Delta H_r^{\ddagger}$ are the enthalpies of activation for *meso* and racemic addition, respectively, P_m is the probability of *meso* addition, and T is the absolute temperature. The difference in the activation entropies is obtained from[3]

$$\Delta(\Delta S_p^{\ddagger}) = \Delta S_m^{\ddagger} - \Delta S_r^{\ddagger} = \mathrm{R} \ln [P_m/1(- P_m)] + \frac{\Delta(\Delta H_p^{\ddagger})}{T} \tag{2}$$

Since the triad fraction P_{rr} in our systems is the most accurately known triad composition, P_m is determined from P_{rr} using

$$P_m = 1 - P_{rr}^{1/2} \tag{3}$$

In Figures 1–4, $-\ln [P_m/(1 - P_m)]$ is plotted against the reciprocal of the absolute temperature (according to eq 1) for the alcohol solvents used. With the exception of methanol, all of the solvent systems give good linear plots; for the methanol system, a straight line is drawn through the data of Figure 1 so that the average enthalpy and entropy differences can be estimated. The values of $\Delta(\Delta H_p^{\ddagger})$ and $\Delta(\Delta S_p^{\ddagger})$ calculated from the slopes of Figures 1–4 with eq 1 and 2 are shown in Table II.

Since the procedure used to obtain $\Delta(\Delta H_p^{\ddagger})$ and $\Delta(\Delta S_p^{+})$ only applies to Bernoullian polymerization[8] the experimental *rm* and *mm* triad fractions are com-

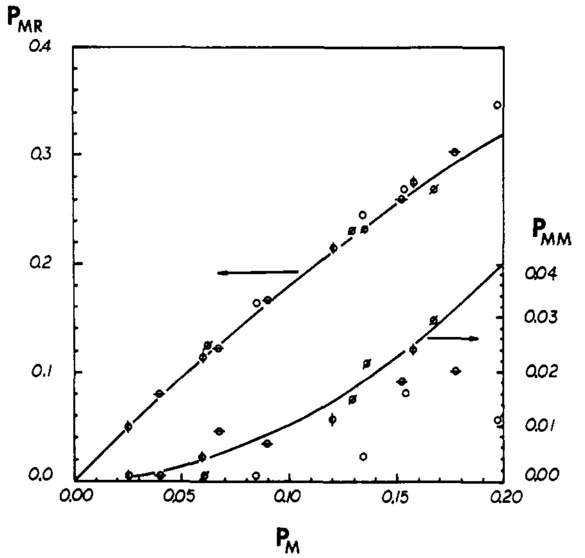

Figure 5. Comparison of experimental *rm* (= *mr*) and *mm* triad fractions with those expected in Bernoullian polymerization: 20% MAA in methanol (O), 1-propanol (-⊖-), and 2-propanol (ϕ); 10% MAA in 1-propanol (∅); theoretical values (—).

pared with the theoretical values in Figure 5, where eq 3 was used to calculate P_m from the experimental *rr* triad fractions. The agreement between the experimental and theoretical triad fractions is good, except for the *mm* triads of polymers prepared in methanol. The α-methyl proton peak in the nmr spectra is small and poorly resolved. In an attempt to improve the resolution of the nmr spectra, several samples were examined at 150° in *o*-dichlorobenzene solution as suggested by Fox and Reinmöller.[6] No significant improvement in the resolution of the *mm* triad peak was observed, and the fraction of *rr* triads and the probability of *meso* addition were in very good agreement with the values obtained from nmr spectra run at 90° in chloroform solution. Thus it must be concluded from these data that the polymerization process is in good agreement, at least to a first approximation, with a Bernoullian model for polymerization in all solvents except methanol. Any higher order effects that may be present in solvents other than methanol are too small to be observed in the experimental triad fractions at 60 MHz. Of course, the values of $\Delta(\Delta H_p^{\ddagger})$ and $\Delta(\Delta S_p^{\ddagger})$ for methanol solvent must be considered only as rough approximations.

The observed solvent effect on the syndiotacticity of the polymer is most probably related to the hydrogen bonding that occurs between the solvent and the polyradical and monomer. The bonded alcohol in some manner directs the addition preferentially toward racemic placement. Since the propagating, hydrogen-bonded species differ for the three solvents used, the enthalpy of activation should be solvent dependent. Indeed, the values of $\Delta(\Delta H_p^{\ddagger})$ (Table II) range from 800 cal in methanol to about 1750 cal in 2-propanol, the magnitude of $\Delta(\Delta H_p^{\ddagger})$ increasing with increasing bulkiness of the alcohol. This relationship between $\Delta(\Delta H_p^{\ddagger})$ and the bulkiness of the alcohol is consistent with a steric effect on the stereoregularity. As the alcohol becomes larger, the strain in the forming bond in the transition state increases. This strain is measured in the $\Delta H_m^{\ddagger}$ and $\Delta H_r^{\ddagger}$ terms. If this effect favors racemic placement, then the $\Delta H_m^{\ddagger}$ term increases more with increasing bulkiness of the alcohol than $\Delta H_r^{\ddagger}$ and therefore $\Delta(\Delta H_p^{\ddagger})$ increases. The difference in the entropy of activation is negative for polymerization in methanol and 1-propanol (Table II), which is expected if a steric effect is the important factor that directs the configuration of the monomer units. However, the large positive $\Delta(\Delta S_p^{\ddagger})$ for polymerization in 2-propanol seems anomalous. One explanation for this positive $\Delta(\Delta S_p^{\ddagger})$ in 2-propanol involves the possibility that the transition state in racemic addition exists with the monomeric acid hydrogen bonded to the carbonyl oxygen of the terminal unit of the polyradical. This condition would lead to a restricted conformation in the transition state for racemic addition that would produce a positive $\Delta(\Delta S_p^{\ddagger})$. The resulting polymer would be more syndiotactic, since the increase in $\Delta(\Delta H_p^{\ddagger})$ with solvent bulkiness overrides the simultaneous increase in $\Delta(\Delta S_p^{\ddagger})$.

The small changes in P_{rr} between 10 and 20% solutions of MAA in 1-propanol indicate that the stereoregularity of the polymer is not strongly dependent upon the concentration of monomer or the extent of conversion for the polymerization conditions used in this study. The twofold dilution in initial monomer concentration produces only about a 2% increase in the fraction of *rr* triads at any given polymerization temperature. An investigation of the relative effects of the initial monomer concentration and the extent of conversion on the stereoregularity of the resulting polymers should indicate whether the hydrogen-bonded monomer or polyradical (or both) is the structure favoring racemic addition. Such a study is beyond the scope of the present investigation, since 100- or 220-HMz spectra would be required to measure accurately such small changes in stereosequencing.

The hydrogen-bonded acid is very similar in structure to the corresponding methacrylate ester, and therefore the tacticity differences observed for the various alcohol solvents could also be present in the esters. Tsuruta and his coworkers[8] have reported that the free-radical addition polymerization of methacrylate esters at 70° results in polymers containing *rr* triad fractions that decrease slightly as the ester group becomes bulkier; they postulate that the hindered rotation about the terminal carbon–carbon bond caused by bulky side chains leads to a more atactic polymer. This explanation can apply to poly(methacrylic acid) only if the restriction on rotation is removed, by assuming a rapid (relative to the rate of propagation) equilibrium between free acid and hydrogen-bonded acid groups at the propagating end of the chain. But this cannot be the case; if such an equilibrium did exist, then no significant solvent effect would be observed. There is some question concerning the triad fractions in the methacrylate esters reported by Tsuruta. The triad fractions were measured from nmr spectra of the poly(methyl methacrylate) samples obtained by hydrolyzing the poly-

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(8) T. Tsuruta, T. Makimoto, and H. Kanai, *J. Macromol. Chem.*, **1**, 31 (1966).

methacrylates in sulfuric acid and then methylating the resulting acid groups. The degrees of hydrolysis were all less than complete and varied considerably from sample to sample. Since the ease of hydrolysis of *meso* and racemic PMMA differ markedly,[9] it is very probable that the residual ester groups in the methacrylates are also mostly racemic. These residual long chain esters may give similar but slightly different chemical shifts in the triad peaks of the nmr spectra; in addition, side chain ester protons of the longer ester groups may appear in the α-methyl region of the nmr spectra, thereby affecting the apparent stereoregularity of the polymers.

In summary, the hydrogen bonding of the alcohol to the monomeric acid and polyradical appears to be responsible for the solvent effects observed on the stereoregularity of the polymer. The thermodynamic quantities which describe the differences in the transition states for *meso* and racemic addition are consistent with an explanation of the role played by the hydrogen-bonded alcohol upon the stereoregularity of the polymer based on steric effects. In addition, a simple technique is presented for obtaining very highly syndiotactic poly(methacrylic acid); to our knowledge, this polymer containing 95% *rr* triads is the most syndiotactic polymer ever synthesized by radiation polymerization.

(9) G. Smets and W. E. DeLoecker, *J Polym. Sci.*, **40**, 203 (1959).

Stereoselectivity and Stereoelectivity in the Copolymerization of Asymmetric Vinyl Ethers

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ABSTRACT: Racemic 1-methylpropyl vinyl ether (I) has been copolymerized with several optically active vinyl ethers, all having an asymmetric carbon atom directly bound to the oxygen atom, in the presence of the stereospecific $Al(O\text{-}i\text{-}C_3H_7)_3$–$H_2SO_4$ heterogeneous catalytic system. When (*S*)-1-phenylethyl vinyl ether (II) or (*R*)-1-phenylethyl vinyl ether (III) or (−)-menthyl vinyl ether (IV) was used as optically active comonomer, the recovered nonpolymerized I was optically active, indicating that the process is stereoelective. The chemical composition and the optical rotation of the fractions, obtained by extracting the polymeric product with boiling solvents, showed that the antipode of I, which according to the stereoelective character of the process was polymerized at higher rate, preferentially gives copolymer with the optically active comonomer; the other antipode gives the homopolymer, in agreement with the stereoselectivity of the process. No clear evidence of stereoselectivity was obtained using $BF_3 \cdot O(C_2H_5)_2$ catalyst in homogeneous phase.

Polymerization of racemic 1-methylpropyl vinyl ether (I) in the presence of the stereospecific catalytic system $Al(O\text{-}i\text{-}C_3H_7)$–$H_2SO_4$ was demonstrated to be stereoselective.[1] In fact, the polymer was separated in fractions having optical activity of opposite sign[1] and the degree of separation obtained was larger than that calculated for a statistical copolymer of the two antipodes.[2,3]

This result indicated that active sites {catalytic complex + growing chain end} able to choose between the antipodes of a racemic vinyl monomer[3] can exist in a catalytic system which does not contain transition metals.

On the other hand, the preferential polymerization of one antipode by an optically active catalyst (stereoelective polymerization)[3] has not yet been achieved in the case of vinyl ethers.

Both the stereoselective and the stereoelective characters of the polymerization of α-olefins by Ziegler–Natta catalysts have been clearly confirmed by copolymerizing a racemic monomer with an optically active one.[4] We have, therefore, applied the same type of investigation in order (i) to confirm the stereoselectivity of the polymerization of racemic vinyl ethers by stereospecific catalyst and (ii) to obtain evidence concerning the possible stereoelectivity of the process.

In the present paper we describe the copolymerization of racemic 1-methylpropyl vinyl ether (I) with (*S*)-(II) or (*R*)-1-phenylethyl vinyl ether (III) in the presence of $Al(O\text{-}i\text{-}C_3H_7)_3$–$H_2SO_4$ catalyst. We report the evidence, given both by chemical composition and optical rotation of polymer fractions and by optical rotation of nonpolymerized I, related to the stereoselective and stereoelective character of the process.

The copolymerization of racemic I with (−)-menthyl vinyl ether (IV) is also reported, together with an experiment of copolymerization of I with III carried out in the presence of $BF_3 \cdot O(C_2H_5)_2$.

Experimental Section

(1) Materials. (a) Alcohols. Racemic 2-butanol, bp 99–100°, $n^{25}\text{D}$ 1.3951, Erba RP, was used as received. (*S*)-2-

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