

Figure 3. Dependence of surface tension at 25° on  $M^{-1}$  for OH-terminated glycols (curve 1) and for Cl-substituted samples (curve 2).

at 80° for monomeric glycols also pass through the broad minimum at the pentamer (see Figure 2). In order to elucidate the origin of this anomaly we have also measured surface tension at 25° both for these glycols as well as for the corresponding liquids in which terminal hydroxyls were substituted with chlorine. It can be seen from Figure 3 that for OH-terminated samples the minimum of  $\gamma^{25}$  has become more pronounced as compared with the corresponding data for 80°, while the values of  $\gamma^{25}$  for Cl-substituted liquids exhibit the typical linear dependence on  $M^{-1}$  for an end-group effect.<sup>2</sup> Thus, it can be safely concluded that the minimum value of  $\gamma$  in OH-terminated glycols is brought about by the competing effects of lowering of the hydrogen-bond concentration and of a simultaneous increase in the chain length. Therefore, absence of such anomaly for Cl-substituted samples suggests that sharp minima of  $\gamma^{80}$  in the high molecular weight region (i.e., at 1300 for PEO and at 2500 for PDA) are not affected by end groups and should be attributed to an intramolecular transition, presumably from an extended into a folded-chain conformation.

It is worth noting that according to the Parachor relation the observed minima in surface tension values would require corresponding density changes in respective samples, whereas our data at 25° for lower (individual) homologs of PEO<sup>14</sup> as well as data of Ingham *et al.*<sup>15</sup> for PEO fractions at 75° show that in the respective series the density is a constant within the claimed experimental uncertainty ( $1.121 \pm 0.002$  g/cm<sup>3</sup> for the former and  $1.080 \pm 0.002$  g/cm<sup>3</sup> for the latter). However, this discrepancy must not be regarded as being crucial as it first seems to be since a Parachor is not a quantitatively exact relation and many deviations are reported in the literature. Therefore, we conclude that this relation may be applied with reasonable accuracy only for those liquids which have similar structural (packing) features (in the case considered here well below and/or above the observed anomalies). If this condition is not satisfied, then the quantitative Parachor equation ceases to apply, although even in such a case a certain correlation between  $\gamma$  and  $\rho$  may still be expected to exist. However, its establishment must wait for further thorough work.

## Summary

The results of experimental studies of surface tension in a series of narrow PEO fractions demonstrate the sensitivity of this parameter to structural changes in undiluted amorphous polymers, which are believed to reflect the transition from extended into folded conformation of macromolecules on the arrival at some characteristic molecular weight interval. Moreover, striking similarity of  $\gamma$ - $M$  dependence for a crystallizing polymer, PEO, and for a noncrystallizable one, PDA, suggests that chain-folding phenomenon is a universal property of both crystallizing and noncrystallizing polymers in the amorphous state.

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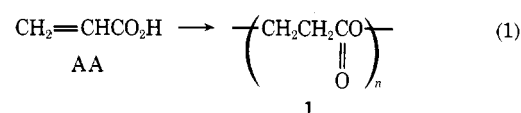
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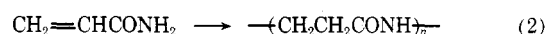
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## Hydrogen-Transfer Polymerization of Acrylic Acid to Poly( $\beta$ -propiolactone)

This paper describes a new finding of the hydrogen-transfer polymerization of acrylic acid (AA) to polyester (1) of  $\beta$ -hydroxypropionic acid.



The hydrogen-transfer polymerization of acrylamide with base catalyst has been reported for the first time by Breslow *et al.*<sup>1</sup> Thus, poly( $\beta$ -alanine) was synthesized from acrylamide (eq 2).



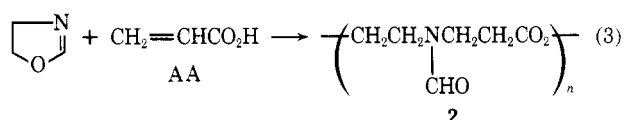
Very recently we have reported alternating copolymerization of 2-oxazoline with AA to give a copolymer of the

**Table I**  
**Hydrogen-Transfer Polymerization of AA at Various Reaction Conditions<sup>a</sup>**

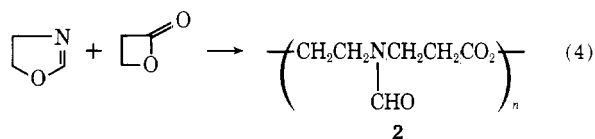
Initiator (mol % for AA)	Temp (°C)	Solvent <sup>b</sup>	Reaction Time (hr)	Polymer Yield <sup>c</sup> (%)	Mol Wt
(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> P (2.5)	100		220	48	1560 <sup>d</sup> (1570) <sup>f</sup> 1240 <sup>e</sup> (1210) <sup>f</sup> 1160 <sup>d</sup> (1450) <sup>f</sup>
(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> P (5.0)	100	Nitrobenzene	300	66	
(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> P (5.0)	120		50	25	
(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> P+CH <sub>2</sub> CH <sub>2</sub> CO <sub>2</sub> <sup>-</sup> (5.0)	100		50	35	
C <sub>6</sub> H <sub>5</sub> N (5.0)	120	<i>p</i> -Xylene	120	37	
C <sub>6</sub> H <sub>5</sub> N (2.5)	100	Nitrobenzene	120	28	696 <sup>d</sup>
(CH <sub>3</sub> ) <sub>3</sub> N+CH <sub>2</sub> CO <sub>2</sub> <sup>-</sup> (5.0)	100		80	35	

<sup>a</sup>Monomer AA, 15 mmol containing 0.075 mmol of *p*-methoxyphenol as a radical inhibitor. <sup>b</sup>Solvent, 1 ml. <sup>c</sup>Crude polymer yield obtained by precipitation of the reaction mixture into a large amount diethyl ether. <sup>d</sup>Determined by nmr spectroscopy before washing with aqueous Na<sub>2</sub>CO<sub>3</sub>. <sup>e</sup>Determined by nmr spectroscopy after washing with aqueous Na<sub>2</sub>CO<sub>3</sub>. <sup>f</sup>Molecular weight determined by vpo in dimethylformamide at 55°.

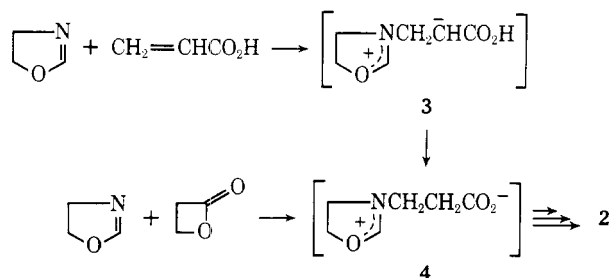
amide ester type structure 2.<sup>2</sup> This reaction (eq 3) provides the



first example of 1:1 alternating copolymerization between cyclic monomer and vinyl monomer. The copolymer 2 was also obtained by alternating copolymerization of 2-oxazoline with  $\beta$ -propiolactone.<sup>3</sup>



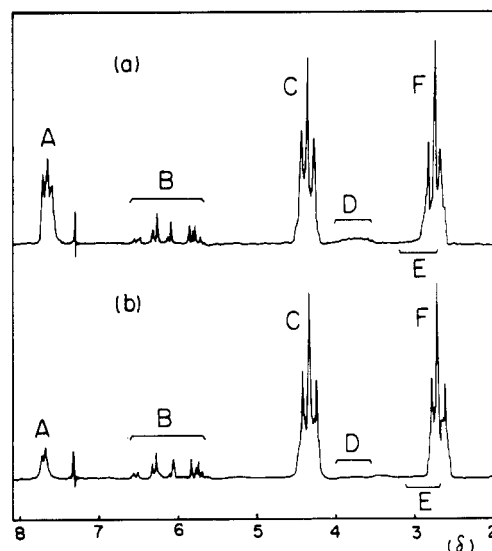
For both of alternating copolymerizations, eq 3 and 4, a betaine 4 in the following scheme was proposed as the common intermediate. The propagation by the polyaddition of betaine 4 gives rise to 2.



In the copolymerization of 2-oxazoline with AA the Michael-type adduct 3 is first formed which is followed by the proton transfer to give 4.<sup>2</sup> Based on these findings we examined the possibility of the proton-transfer process in the reaction of AA and we now disclosed a new mode of polymerization of AA (eq 1).

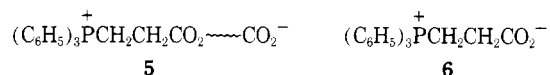
In a tube under nitrogen 0.375 mmol of triphenylphosphine was added as a catalyst to AA (15 mmol) containing *p*-methoxyphenol (0.075 mmol, a radical inhibitor). The tube was sealed and kept for 220 hr at 100° in the dark. Then, the reaction mixture was poured into a large amount of diethyl ether to precipitate polymer. The polymer was separated and dried *in vacuo* at room temperature. White powdery polymer was obtained in 48% yield (0.52 g).

Nmr spectrum of the polymer (Figure 1a) clearly shows the structure of polyester of  $\beta$ -hydroxypropionic acid, poly( $\beta$ -propiolactone) (1). Triplet-like signals, C ( $\delta$  4.33)



**Figure 1.** Nmr spectra of the polymer obtained from AA by triphenylphosphine in CDCl<sub>3</sub> (a) before washing and (b) after washing with 1 *N* aqueous Na<sub>2</sub>CO<sub>3</sub> solution.

and F ( $\delta$  2.60), are due to the protons of O—CH<sub>2</sub> and CH<sub>2</sub>CO<sub>2</sub> groups, respectively, whose assignments agree with those of poly( $\beta$ -propiolactone) as reported previously.<sup>3</sup> Besides them, multiplet signals, A, B, D, and E are seen. Peak A at  $\delta$  7.7 is assigned to phenyl protons of (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>P<sup>+</sup> species. Multiplet B at  $\delta$  6.5~5.6 is due to vinyl protons of alkyl acrylate CH<sub>2</sub>=CHCO<sub>2</sub>R. Finally, broad multiplets D and E are assigned respectively to  $\beta$ - and  $\alpha$ -methylene protons of <sup>+</sup>PC <sup>$\alpha$</sup> H<sub>2</sub>C <sup>$\beta$</sup> H<sub>2</sub>CO<sub>2</sub> in the phosphobetaine-type species, 5.



In relation to the phosphobetaine species 5, the betaine 6 was quantitatively prepared in this study from triphenylphosphine and AA, mp 188° (lit.<sup>4</sup> mp 186°). In the nmr spectrum of 6 thus obtained the protons of CH<sub>2</sub>CO<sub>2</sub><sup>-</sup> appear at the same region of D and the protons of P<sup>+</sup>CH<sub>2</sub> appear at E region as a broad multiplet.

Based on the assumption that one molar equivalent of (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>P<sup>+</sup> group corresponds to one polymer molecule, the degree of polymerization ( $\overline{P}_n$ ) was calculated to be  $n = 17.4$  (mol wt 1560) from the integration ratio of signals C and A, respectively. The vapor pressure osmometry (vpo) molecular weight of the polymer was 1570. Both

data obtained by these methods agreed well with each other.

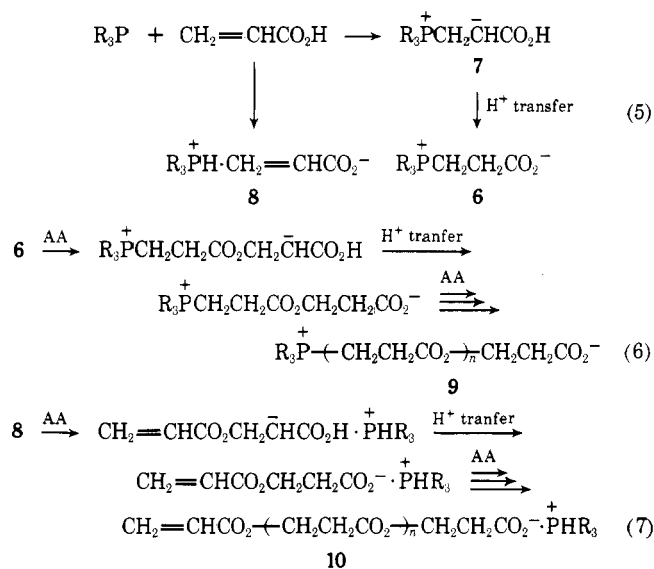
The same sample polymer was dissolved in  $\text{CHCl}_3$ , washed two times with 1 *N* aqueous  $\text{Na}_2\text{CO}_3$  solution, and washed additionally two times with water. Then, the polymer was precipitated by pouring the chloroform solution into a large amount of diethyl ether. Nmr spectrum of the washed polymer (Figure 1b) shows that peaks A, D, and E were diminished remarkably, although they did not disappear. On additional washing, peaks A, D, and E did not decrease any more. Peak B was not changed with washing. This strongly indicates that a part of the  $(\text{C}_6\text{H}_5)_3\text{P}^+$  species is chemically bound to polymer. The molar ratio of the integration of peak A (15 H) and B (3 H) was 1.0:4.0. On the basis of the assumption that 1 molar equiv of  $(\text{C}_6\text{H}_5)_3\text{P}^+$  and  $\text{CH}_2=\text{CHCO}_2$  groups are attached at the polymer end, the degree of polymerization was calculated to be  $n = 16.5$ , which corresponded to the molecular weight of 1240. A close value of the molecular weight of 1210 was obtained by vapor pressure osmometry (Table I). The decrease of the molecular weight was due to the loss of  $(\text{C}_6\text{H}_5)_3\text{P}^+$  group by washing with the  $\text{Na}_2\text{CO}_3$  solution.

The spectrum of the polymer supports a structure of poly( $\beta$ -propiolactone), *i.e.*, characteristic bands appear at 1740, 1170, and 1020  $\text{cm}^{-1}$  indicating the presence of the  $\text{CO}_2$  group. Furthermore, no carboxyl group was detected in nmr and ir spectra of the polymer. This shows no occurrence of the vinyl polymerization by radical or anionic mechanism.

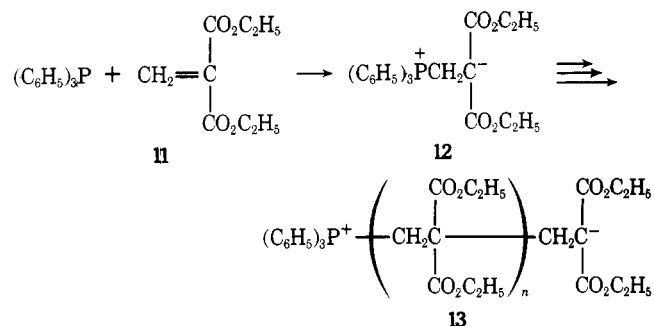
This type of AA polymerization was induced not only by triphenylphosphine but also by other bases such as pyridine. In addition, betaines **6** and  $(\text{CH}_3)_3\text{N}^+\text{CH}_2\text{CO}_2^-$  were effective for the hydrogen-transfer polymerization of AA. The reaction can be carried out with or without solvents (Table I).

From the above findings the following mechanism is tentatively given for the phosphine-catalyzed system. The Michael-type adduct **7** (Scheme.I) is first formed as an intermediate which is followed by a proton transfer (probably through an intermolecular mechanism) to give the phosphobetaine **6**. The betaine **6** is in equilibrium with phosphonium acrylate (**8**) under the polymerization conditions, *e.g.*, at reaction temperatures of above 100°. It may also be possible that **8** is formed directly from initiator and AA. When initiation is induced by **6** polymerization proceeds *via* the so-called macrozwitterion **9**<sup>5</sup> as given by eq 6. On the other hand, initiation by acrylate anion **8** leads to **10** (eq 7). In both mechanisms eq 6 and 7, polymer grows by the repetition of the formation of Michael-type adduct between AA and propagating carboxylate anion which is followed by proton transfer. When the polymer has a structure of **9**, (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>P<sup>+</sup> group will remain even after washing with 1 *N* aqueous Na<sub>2</sub>CO<sub>3</sub> solution. On the other hand, (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>P<sup>+</sup> group in the polymer of a structure **10** will be washed out by treatment with Na<sub>2</sub>CO<sub>3</sub> solution.

### Scheme I



As to the macrozwitterion mechanism, only one case has been known so far in the polymerization of the vinyl monomer. Jaacks and Franzmann<sup>6</sup> have recently reported that the polymerization of diethyl methylenemalonate (11) by triphenylphosphine initiator proceeds *via* the macrozwitterion (13) involving the first betaine species (12). This may be interestingly compared with the present findings.



More detailed studies on the hydrogen-transfer polymerization of AA are being undertaken.

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