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The Fundamental Basis for Cyclopolymerization. V. A Kinetically Based Explanation for the Enhanced Rate*

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SUMMARY

The enhanced rate of cyclopolymerization of divinyl monomers over that of the corresponding monovinyl monomers is considered. The relative polymerization rates of the following monovinyl-divinyl monomer pairs were determined: methyl methacrylate-methacrylic anhydride; 2-cyano-1-heptene–2,6-dicyano-1,6-heptadiene; and 2-phenyl-1-heptene–2,6-diphenyl-1,6-heptadiene. An attempt was made to prepare methacrylic isobutyric anhydride as the monovinyl monomer to compare with methacrylic anhydride but its inherent instability precluded its isolation in pure state. The over-all rate of the divinyl monomer in every case was considerably greater than that of the corresponding monovinyl monomer, the ratios varying from two to ten. From the rate data obtained it was possible to estimate the effective concentration of the intramolecular double bond with respect to the radical, and values greater than 20 M at 50° were obtained in the case of 2,6-dicyano-1,6-heptadiene. This value compares favorably with a concentration of 21.8 M for liquid ethylene at -102°. These results can be interpreted most satisfactorily in terms of a concerted cyclization step which requires considerable preorientation prior to reaction. This favorable preorientation could be interpreted as an electronic interaction between the developing radical cite and the intramolecular double bond.

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INTRODUCTION

It is well known that the rate of cyclopolymerization of divinyl monomers is greater than that of the corresponding monovinyl monomers. Although several studies concerning the rate of cyclopolymerization have been reported [1-6], the above special feature of cyclopolymerization has not been considered from a kinetic standpoint nor an attempt made to explain it. Since the process includes at least two kinds of growing polymer radicals and the several possible reactions of each, analysis of the mechanism in an exact way is difficult. In addition to this, the fact that precipitation of the polymer in the medium often results during the cyclopolymerization may make the analysis much more difficult. This problem arises because the precipitate often occludes the growing polymer radicals and interferes with the termination reactions. Accordingly, several assumptions and approximations will be necessary for the analysis to be meaningful.

In the present paper, the over-all rates of cyclopolymerization of methacrylic anhydride (MA), 2,6-dicyanoheptadiene-1,6 (DCH), and 2,6-diphenylheptadiene-1,6 (DPH) are presented. The rate constants are calculated using a derived rate equation. In an attempt to arrive at a solution of the above problem a comparison of the rates of the divinyl monomers with the rates of the corresponding monovinyl monomers has been made.

Kinetics of Cyclopolymerization of Symmetrical Divinyl Monomers

The process of cyclopolymerization of a symmetrical divinyl monomer by a free radical mechanism involves the following elementary reactions:

Initiation

$$I \xrightarrow{k_d} 2I\cdot \tag{1}$$

$$I\cdot + M \xrightarrow{k_i} M_i^{\cdot} \tag{2}$$

Propagation

$$M_i^{\cdot} \xrightarrow{k_c} M_c^{\cdot} \qquad \text{(Cyclization)} \tag{3}$$

$$M_i^{\cdot} + M \xrightarrow{k_{p1}} M_i^{\cdot} \tag{4}$$

$$M_c^{\cdot} + M \xrightarrow{k_{p2}} M_i^{\cdot} \tag{5}$$

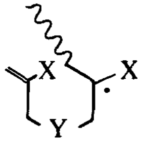
Termination

$$M_i^{\cdot} + M_i^{\cdot} \xrightarrow{k_{11}} P \tag{6}$$

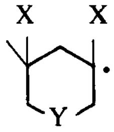
$$M_i^{\cdot} + M_c^{\cdot} \xrightarrow{k_{12}} P \tag{7}$$

$$M_c^{\cdot} + M_c^{\cdot} \xrightarrow{k_{22}} P \tag{8}$$

In the above reaction, I, M, and P represent an initiator, a monomer, and a stable polymer molecule, respectively. $M_i^{\bullet}$ and $M_c^{\bullet}$ represent a noncyclized and a cyclized polymer radical as follows:



$M_i^{\bullet}$



$M_c^{\bullet}$

k_d, k_i, k_c, k_p, k_{p2}, k_{11}, k_{12}, and k_{22} represent the rate constant for decomposition of the initiator, initiation, cyclization, propagation of $M_i^{\bullet}$, propagation of $M_c^{\bullet}$, termination reactions between $M_i^{\bullet}$ and $M_i^{\bullet}$, $M_i^{\bullet}$ and $M_c^{\bullet}$, and $M_c^{\bullet}$ and $M_c^{\bullet}$, respectively.

In order to derive the rate equation, the steady-state assumption was made and the following relationship can be obtained:

$$fkd[I] = k_{11}[M_i^{\bullet}]^2 + K_{12}[M_i^{\bullet}][M_c^{\bullet}] + k_{22}[M_c^{\bullet}]^2 \qquad (9)$$

where f represents efficiency of the initiator. If the cross-termination ratio ϕ, is unity (this is justified by the similar structures of $M_i^{\bullet}$ and $M_c^{\bullet}$), namely, if the following relationship is assumed,

$$\phi^2 \equiv \frac{(k_{12}/2)^2}{K_{11} \cdot k_{22}} = 1; \quad \text{or} \quad k_{12}{}^2 = 4k_{11}k_{22} \ [7] \qquad (10)$$

then Eq. (9) may be written as

$$(fk_d[I]/k_{22})^{1/2} = \alpha[M_i^{\bullet}] + [M_c^{\bullet}] \qquad (11)$$

where

$$\alpha^2 = k_{11}/k_{22} \qquad (12)$$

In the above chain propagations, if the kinetic chain length is long enough, then

$$k_c[M_i^{\bullet}] = k_{p2}[M_c^{\bullet}][D] \qquad (13)$$

may be assumed by application of the steady-state assumption to $M_c^{\bullet}$ in the chain propagation, in which [D] represents the concentration of double bond of the monomer and equals twice the concentration of the monomer.

From Eqs. (11) and (13), the concentration of the two free radicals can be derived as follows:

$$[M_c^{\bullet}] = (fkd[I]/k_{22})^{1/2}\frac{k_c}{\alpha k_{p2}[D] + k_c} \tag{14}$$

$$[M_i^{\bullet}] = (fkd[I]/k_{22})^{1/2}\frac{k_{p2}[D]}{\alpha k_{p2}[D] + k_c} \tag{15}$$

Hence the rate of polymerization is given by

$$R_p = -\frac{d[D]}{dt} = k_{p1}[M_i^{\bullet}][D] + K_c[M_i^{\bullet}] + k_{p2}[M_c^{\bullet}][D] \tag{16}$$

The rate of polymerization, R_p, is obtained as follows:

$$R_p = (fkd/k_{22})^{1/2}k_{p2}[I]^{1/2}[D]\frac{2k_c + k_{p1}[D]}{k_c + dk_{p2}[D]} \tag{17}$$

If k_c is not zero, Eq. (17) can be developed as follows:

$$R_p = k_{p2}(fkd/k_{22})^{1/2}[I]^{1/2}[D] \quad 2 + \frac{(k_p - 2\alpha k_{p2})[D]}{k_c} - \frac{(k_{p1} - 2\alpha k_{p2})\alpha k_{p2}[D]^2}{k_c^2} \tag{18}$$

Cyclopolymerization may be characterized by the fact that the cyclization reaction (3) is faster than the propagation reaction (4); in other words, $k_{p1}[D]$ is smaller than k_c at the usual concentration of monomer. If $k_{p1}[D]$ is comparable with $k_{p2}[D]$ and α is nearly unity, then $\alpha k_{p2}[D]$ is smaller than k_c. Therefore, Eq. (18) can be approximated as

$$R_p = k_{p2}(fkd/k_{22})^{1/2}[I]^{1/2}[D]\left[2 + \frac{k_p - 2\alpha k_{p2}}{k_c}[D]\right] \tag{19}$$

Eq. (19) shows that $R_p/[I]^{1/2}[D]$ is a linear function of [D] and independent of (I), and that $k_{p1}/\sqrt{k_{11}}$ and $k_{p2}/\sqrt{k_{22}}$ can be calculated from R_p and k_{p1}/k_c.

The meaning of the coefficient 2, which is the first term in the parentheses of Eq. (19), is very important. It comes from the fact that the cyclization step (3) and the propagation step (5) have the same rate as shown in Eq. (13), since these reactions occur alternately and simultaneously. Since the major part of the growing radical is $M_c^{\bullet}$ in the usual cyclopolymerization as shown in Eq. (14) and (15), the rate of cyclopolymerization appears to be about twice as fast as the usual polymerization, even though the over-all rate constants of cyclopolymerization are nearly the same as those of usual polymerization. This is assumed to be the first and the most fundamental reason why cyclopolymerization is so much faster than polymerization of the corresponding monovinyl monomers.

It should be emphasized that the homogeneity of the cyclopolymerization mixture is important for application of Eqs. (17) or (19). If precipitation of the polymer in the mixture is observed during the polymerization, the rate will often be accelerated abnormally. The equations cannot be applied to such a system.

RESULTS AND DISCUSSION

The over-all rate of polymerization of MA and DCH initiated by azobisisobutyronitrile (AIBN) were measured dilatometrically in dimethyl formamide (DMF) at different temperatures. The results are shown in Tables 1 and 2.

In the polymerization of MA in DMF, the polymerization mixture became cloudy at even low conversion of the monomer; however, the polymer obtained was soluble in DMF. It is assumed that PMA is less soluble in the mixture of DMF and MA. On the contrary, PDCH was completely soluble in the mixture of DMF and DCH below 3 mole/l of the monomer.

In spite of the greatest degree of care taken in the experiments, the rate of MA was proportional to $[I]^{0.60}$ as shown in Fig. 1. Smets [1, 5] has obtained similar results in polymerization of acrylic anhydride in cyclohexanone or DMF, and has attributed them to occlusion of the growing polymer radical by the precipitated polymer since it was possible to observe the trapped free radical by ESR. However, Gibbs [2] obtained a somewhat different result for the rate of MA in DMF. The rate was proportional to the half power of the concentration of the initiator. Accordingly, other solvents, dimethyl sulfoxide, N-methyl pyrrolidone, and tetramethylenesulfone, were tested as possible substitutes for DMF, but none of them were better than DMF.

The rate of DCH was proportional to the half power of the concentration of AIBN within experimental error as shown in Fig. 1.

In Fig. 2, $R_p/[I]^{1/2}[D]$ were plotted against [D]. A fairly good linear

Table 1. Rate of Polymerization of Methacrylic Anhydride

Temp (°C)	[D] (mole/l)	[I] (mole/l × 10^2)	R_p (mole/l sec × 10^5)	R_p[I] [D] ($l^{1/2}$/mole$^{1/2}$ sec × 10^4)
35	1.95	0.975	1.028	0.534
	2.97	0.97	1.644	0.559
	4.48	0.98	2.530	0.571
	5.96	0.98	3.938	0.668
	7.48	0.98	5.22	0.704
50	1.96	0.098	1.94	3.16
	1.96	0.098	2.01	3.29
	1.95	0.195	2.94	3.42
	1.95	0.49	5.12	3.60
	1.95	0.98	8.40	4.36
	1.96	0.98	8.14	4.19
	1.96	1.96	11.98	4.38
	0.74	0.98	3.22	4.38
	0.75	0.98	3.22	4.33
	1.50	0.98	6.14	4.14
	3.00	0.98	13.00	4.38
	4.50	0.98	20.40	4.57
	6.00	0.98	28.20	4.73
	7.46	0.98	35.40	4.80
	2.97	0.195	4.80	3.65
	4.48	0.195	7.80	3.94
	7.48	0.195	14.24	4.31
	10.48	0.196	20.80	4.48
60	1.03	0.98	11.86	11.58
	1.49	0.98	17.12	11.58
	1.96	0.98	23.64	12.18
	2.99	0.98	37.94	12.78

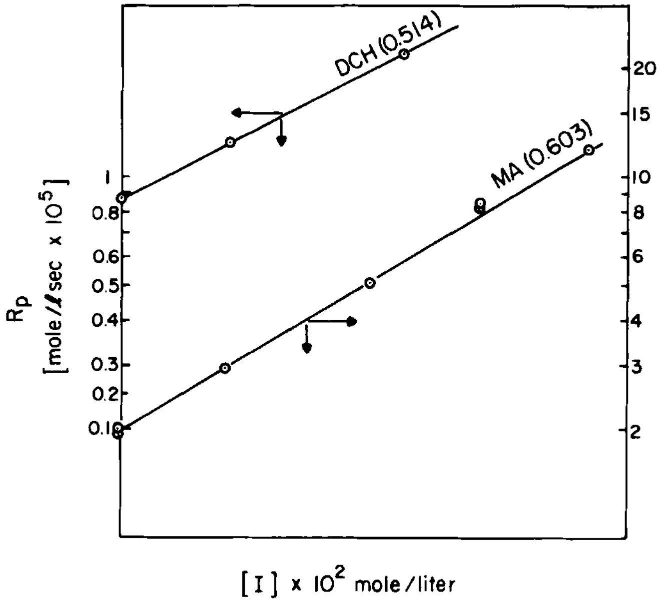


Fig. 1. Relationship of R_p and [I].

Table 2. Rate of Polymerization of Dicyanoheptadiene

Temp (°C)	[D] (mole/l)	[I] (mole/l × 10^2)	R_p (mole/l sec × 10^5)	R_p[I] [D] ($l^{1/2}$/mole$^{1/2}$ sec × 10^5)
40	1.47	2.00	0.418	2.01
	4.42	2.00	0.962	1.54
50	1.48	1.00	0.877	5.91
	1.48	2.01	1.250	5.95
	1.48	6.02	2.20	6.04
	2.22	1.00	1.250	5.63
	2.96	1.00	1.625	5.48
	4.45	1.00	2.22	4.99
	5.93	1.00	2.58	4.36
60	1.48	1.00	2.63	17.75
	4.47	1.01	6.69	14.95

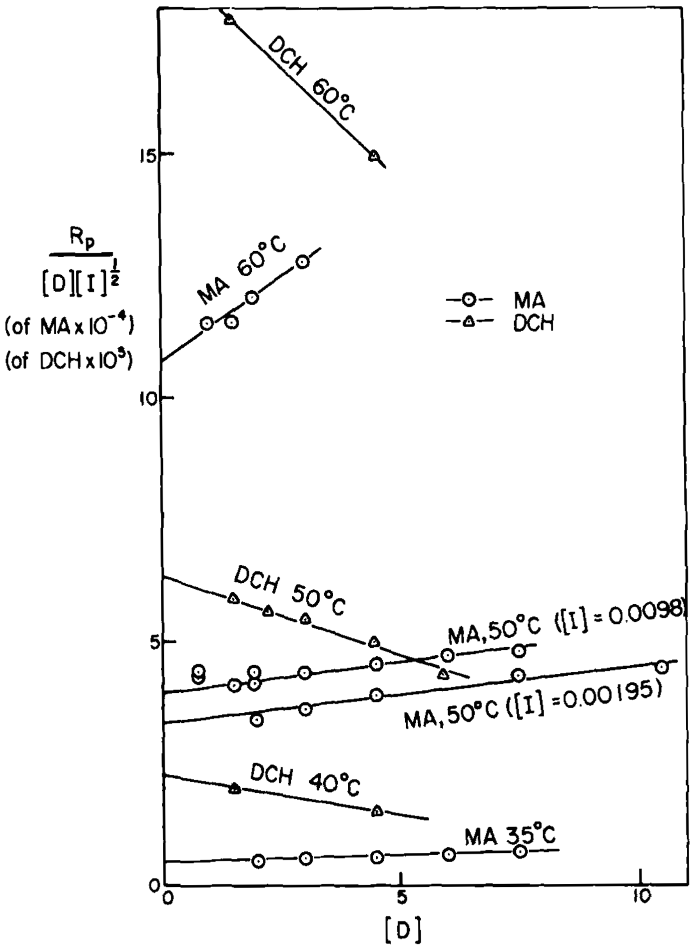


Fig. 2. Relationship between $R_p/[D]\,[I]^{1/2}$ and [D].

relationship was obtained. From the intercepts and the slopes, $k_{p2}/\sqrt{k_{22}}$ and $\alpha k_{p2}/k_c$ can be calculated. For the calculation the values of k_d and f for AIBN as shown in Table 3 were used. Then $k_p/\sqrt{k_{22}}$ ratio was calculated using the ratio, k_{p1}/k_c, which was determined from the residual unsaturation of the polymers. These are summarized in Table 4.

In the polymerization of MA at 50°C, two sets of data were obtained at different concentrations of AIBN. However, the two sets did not coincide

Table 3.

Temp (°C)	Rate f[8]	Constant for Decomposition of AIBN $k_d \times 10^6$ [9] (sec^{-1})
35	0.6	0.174
40	0.6	0.402
50	0.6	1.99
60	0.6	8.94
97	0.6	1150

Table 4. Over-all Rate Constants of MA and DCH

Monomer Temp (°C)	$k_{p2}/\sqrt{k_{22}}$[a] (1/mole sec)$^{1/2}$	$\alpha k_{p2}/k_c$ (1/mole)	k_{p1}/k_c (1/mole)	$k_{p1}/\sqrt{k_{11}}$ (1/mole sec)$^{1/2}$
MA 35	0.0694	0.070	0.251 [26]	0.249
50	0.179	0.070	0.207	0.528
60	0.228	0.032	0.182	1.30
DCH 40	0.0229	0.071-0.074	0.007	0.0022
50	0.0291	0.049-0.052	0.007	0.0039
60	0.0414	0.049-0.052	0.007	0.0056

[a] Activation energy of k_{p2}/k_{22}: MA, 8.8 ± 3.7 kcal/mole; DCH, 6.2 ± 1.4 kcal/mole.

with each other. The data at 0.98×10^{-2} mole/l of [I] were used for the above calculation. Therefore, the rate constants of MA include some deviation which results from the deviation from the root square law.

2-Cyanoheptene-1 (CH), 2,6-diphenylheptadiene-1,6 (DPH), 2-phenylheptene-1 (PH), and α-methyl sytrene were polymerized in test tubes sealed under high vacuum, and the polymers produced were weighed. The rate constants are shown in Table 5. The rate constant of DPH was calculated by assuming $2k_{p2}/\sqrt{k_{22}}$ equals $R_p/(fk_d)^{1/2}[I]^{1/2}[D]$.

Cyclopolymerization may be characterized by the larger rate constant of the cyclization reaction than that for the propagation of $M_1^{\cdot}$. As mentioned above, the rapid rate of the cyclization will result in about twice the over-all rate of polymerization of the corresponding monovinyl monomer, even though the over-all rate constants may be similar. However, the problems in some instances are to find a suitable monovinyl monomer for use in a reliable comparison of their rate constants. This paper presents one way for resolving the problems using the data obtained.

The first consideration involves the steric effect of the substituent of the radical carbon atom on its reaction. The radical $M_1^{\cdot}$ in the polymerization mixture will be surrounded by the double bond of the same molecule, which may sterically hinder the reaction of $M_1^{\cdot}$ with the double bonds of other monomer molecules, while it may react with the double bond of the same molecule with less steric hinderance (Fig. 3). In other words, since the collision frequency of $M_1^{\cdot}$ with the double bond of the same molecule may be greater than the frequency of collision with the double bond of another molecule, it is reasonable to expect that the rate of the former reaction may be greater than the latter.

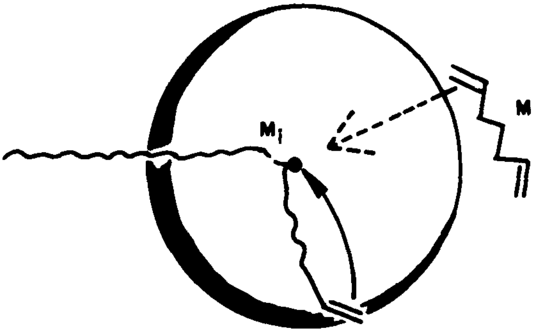


Fig. 3. Steric effect of the substituent of the radical carbon atom $M_1^{\cdot}$ on its reaction.

Therefore if the probabilities of their reactions are calculated assuming their collision frequencies to be the same, the results may not coincide with the experimental results. The ratio of the probabilities of Reactions (3) and (4) have been calculated assuming the collision frequencies to be the same, and the ratio was quite different from the observed values in cyclopolymerization [10].

It is well known empirically that the steric effect of an alkyl group attached to the radical carbon atom is very great in polymerization. Tsuruta

Table 5. Over-all Rate of Several Monomers

Monomer	Temp (°C)	[D] (mole/1)	[I] (10^2 mole/1)	Solvent	$k_p/\sqrt{kt}$ (1/mole sec)$^{1/2}$	Appearance of Polymer
Cyanoheptene	60	3.0	1.75	DMF	0.71×10^{-4}	Liquid
Diphenylheptadiene	97	3.0	1.75	Xylene	0.63×10^{-4}	Solid
Phenylheptene	97	2.6	1.75	Xylene	0.12×10^{-4}	Liquid
α-Methyl Styrene	97	3.0	1.75	Xylene	0.00	–

and Chikanishi have reported that the over-all rates of polymerization of α-alkyl acrylates were remarkably decreased with increasing steric effects of the α-alkyl group [11]. Conversions of methyl α-ethyl-, methyl α-propyl-, and methyl α-butylacrylates were 5-12%, 3%, and trace, respectively, at 65-80°C for 15 days. They have attributed the decrease of the rate to the steric effect of the α-alkyl group, since a linear relationship between the relative reactivity of the α-alkylacrylates toward styryl radical and Taft's steric parameter was observed.

The above steric effect has also been observed in α-alkyl acrylonitriles. Methacrylonitrile can be easily polymerized while α-ethylacrylonitrile cannot be polymerized [12]. This may be due to the greater steric effect of the ethyl group.

Accordingly, the scheme of Table 6, which shows model free radicals for comparison with the radicals in cyclopolymerization of MA and DCH, might be considered.

The rate of polymerization of the models in Table 6 would be expected to be similar to the rates of reaction of the radicals of MA and DCH, with the exception of the reaction of $M_1^{\cdot}$ with the double bond of the other molecule. In the above discussion the steric hinderance for the double bond of the monomer was neglected. It can be neglected in divinyl monomers, but not in monovinyl monomers such as methacrylic isobutyric anhydride (MIA) and CH. Accordingly, the rate constant $k_{p1}/\sqrt{k_{11}}$ of MA and DCH would be expected to be greater than $k_p/\sqrt{kt}$ of MIA and CH, respectively.

Among these models, only MMA is not a good model from the standpoint of electric charge of the double bond. The e values of MA and MMA have been reported as +1.1 [5] and +0.4, respectively. However, a better model could not be found. From the standpoint of steric effects, the difference between $M_c^{\cdot}$ and MMA radical may not be important, since it has been shown that the steric effect of the alkyl group of alkyl methacrylates is not as important as that of the alkyl group of methyl 2-alklacrylates [13].

Table 7 shows $k_{p2}/\sqrt{k_{22}}$ of MA in comparison with $k_p/\sqrt{k_t}$ of MMA.

Table 8 shows a comparison of $k_{p2}/\sqrt{k_{22}}$ of DCH and $k_p/\sqrt{k_t}$ of MAN. The value of DCH is seen to be in good accord with that of the model, while that of MA is not. There are several possible reasons for the contrast between MA and MMA. The first one is that MMA is not a good model from the viewpoint of the charge on the double bond. The second one is that a little deviation of the value from the theoretical basis can be predicted because of the heterogeneity of the polymerization mixture. The third one, which may be the most important, is concerned with the resonance stability of the cyclized radical.

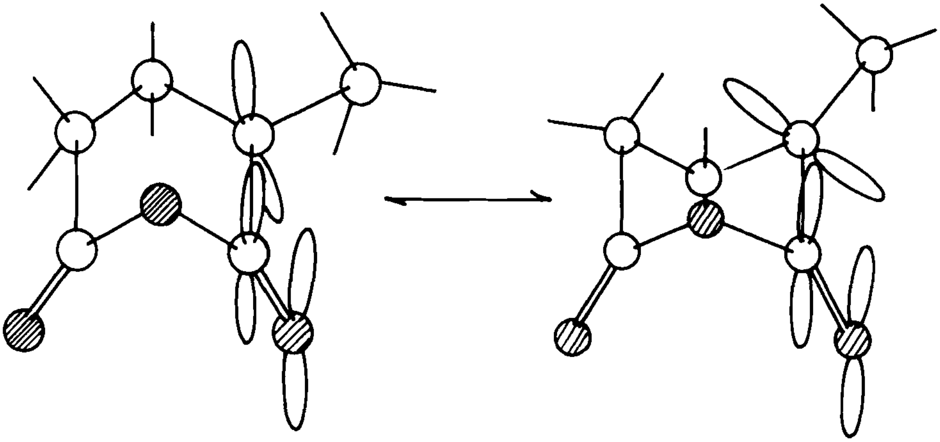
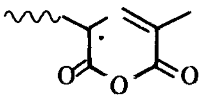
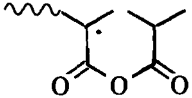
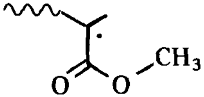
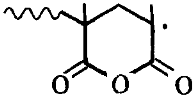
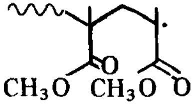


Fig. 4. Chair (right) and boat (left) conformations of the cyclized radical of MA. Open circles represent carbon atoms and shaded circles represent oxygen atoms.

The two main conformations in the cyclized radical of MA would be expected to be the chair and boat conformations (Fig. 4). However, on the other hand, the ratio of chair to boat conformations of cyclohexane-1,4-dione is 80:20 [17]. Since the introduction of an oxygen atom instead of a carbon atom does not affect the ring conformation so much, the anhydride ring conformation would be expected to be similar to that of cyclohexanedione. The boat conformation of cyclohexane-1,4-dione is twisted a little because of 1,4-dipolar repulsion of the carbonyl groups. Assuming the cyclized radical of MA to take the same conformation, the π-orbitals of the sp^2 carbon of the radical and the carbonyl group attached to it are parallel only in the nontwisted boat form but are not parallel in the chair form and the twisted boat form. The probability of existence of the nontwisted boat form must be very small, which means that the resonance $\dot{C}-C=O \leftrightarrow C=C-\dot{O}$ must be restricted by the ring conformation. These effects would result in an unusual increase in the reactivity of the cyclized radical from MA.

On the other hand, the conjugated CN group is outside of the ring in the cyclized radical of DCH. Resonance stabilization of the radical by the nitrile group is not affected by the ring conformation. The effect of introduction of an sp^2 carbon into the cyclohexane ring derived from DCH on the reactivity of the radical may be very small.

Table 6

Monomer	Radical	Reaction	Model
MA	$M_i^{\cdot}$ 	With double bond of other molecule	Methacrylic isobutyric anhydride (MIH) 
		With double bond of the same molecule	Methyl methacrylate (MMA) 
	$M_c^{\cdot}$ 	With double bond	MMA 

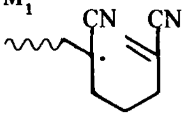
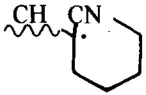
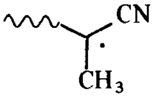
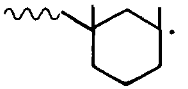
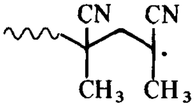
DCH	$M_i\cdot$ 	With double bond of other molecule	
		With double bond of the same molecule	Methacrylonitrile (MAN) 
	$M_c\cdot$ 	With double bond	MAN 

Table 7. Comparison of Rate Constants of MMA and MA

$k_p/\sqrt{k_t}$ of MMA $(l/\text{mole sec})^{1/2}$		$k_{p2}/\sqrt{k_{22}}$ of MA $(l/\text{mole sec})^{1/2}$	
0.050	(35.9°C) [14]	0.069	(35°C)
0.070	(50.5°C) [14]	0.179	(50°C)
0.120	(60°C) [15]	0.228	(60°C)

Table 8. Comparison of Rate Constants of MAN and DCH

$k_p\sqrt{k_t}$ of MAN [16] $(l/\text{mole sec})^{1/2}$		$k_{p2}/\sqrt{k_{22}}$ of DCH $(l/\text{mole sec})^{1/2}$	
0.0383	(60°C)	0.0414	(60°C)

These discussions can explain the results shown in Tables 7 and 8, and may support the proposed mechanism and Eq. (19).

From the above scheme, $k_{p1}/\sqrt{k_{11}}$ of DCH and MA should be greater than $k_p/\sqrt{k_t}$ of CH and MIA. This was supported by the data of DCH and and CH shown in Tables 3 and 4. However, the preparation of MIA was unsuccessful as described in the Experimental Section. The rate constant $k_p/\sqrt{k_t}$ of isobutyl methacrylate was given at 0.151 [18] at 60° while $k_p/\sqrt{k_{11}}$ of MA, 1.30, was very much larger. However, we have no basis on which to discuss the difference further.

By similar reasoning, the rate constant for the reaction of $M_i^{\bullet}$ with the double bond of another molecule of DPH, $k_p/\sqrt{k_t}$, should be greater than that of PH, and that of $M_c^{\bullet}$ of DPH should be similar to that of α-methyl styrene. In other words, the order of the rate constants $k_p/\sqrt{k_t}$ should be as follows:

$$\text{DPH} \simeq \alpha\text{-methyl styrene} \gg \text{PH}$$

However, the result as shown in Table 4 shows the following order:

$$\text{DPH} > \text{PH} > \alpha\text{-methyl styrene}$$

The reason for this order may be explained in the following way: In the above discussion the polar effect of the substituent toward the propagation was neglected, because the difference of the effect between methyl group and the ring component was very small. Hammett's σ_{para} constants for methyl, ethyl, and isopropyl have been given as -0.170 ± 0.02, - 0.151 ± 0.02, and -0.151 ± 0.02 [19]. If σ_{para} for hexyl or cyclohexyl is the same as for ethyl and isopropyl, the difference between methyl, 0.019, may be too small to contribute to the reactivity of the polymer radical.

It is well known in vinyl polymerization that a vinyl monomer is more easily attacked by a radical which has opposite charge. Since the charge of the polymer radical and monomer should be nearly the same in homopolymerization, there should exist some range of charge of the monomer which can polymerize by a radical mechanism. This range has been reported as $1.7 > e > -1.0$ or $0.7 > \sigma > -0.1$ [20], where e and σ mean Alfrey-Price's constant and Hammett's constant, respectively, for the substituent on the vinyl group.

The e values of MMA and MAN are 0.4 and 0.9-1.3 and located near the center of the range. Accordingly, a small change in the charge may not affect their reactivity so much. However, for a monomer whose e value is located near the boundary of the range, a small change in the charge may result in a large change in the reactivity. Consideration of the change in the charge of a polymer radical or monomer will be very important for such a monomer.

α-Methyl styrene does not homopolymerize through a radical mechanism but does copolymerize with other monomers. The reasons as described in the literature [21] are that α-methyl styrene becomes more negative by substitution of an α-hydrogen atom of styrene with a methyl group and that the allylic hydrogen atoms promote chain-transfer reaction. The e value of α-methyl styrene is given as -1.2 (with MMA), -1.1 (with AN), or -0.8 (with MAN) [22]. Since the value is located near the boundary of the range, the first reason may account for the result. On the contrary, α-pentyl styrene (2-phenylheptene-1) polymerized very slowly and gave liquid polymer as shown in Table 4, while α-methyl styrene did not polymerize under the same conditions. This suggests that the chain-transfer reaction of the polymer radical to monomer may not be the reason that α-methyl styrene does not polymerize, that the steric effect of the methyl group may not be the reason, and that only the polar effect may be the reason.

The difference of Hammett's σ between methyl and pentyl group is 0.019, which corresponds to 0.05 in the difference of e [22]. It is assumed that such a small difference of the charge of the radical has a large effect on the polymerizability of α-alkyl styrenes.

In spite of the low polymerizability of α-methyl styrene and 2-phenylheptene-1, DPH polymerized to give solid polymer. A possible explanation is that the reactivity of the cyclized radical of DPH will be much higher than α-methyl styrene because of the decreased negativity.

Relationship of Cyclization Rate of Over-all Rate

In a two-step process in which the individual rates of the two steps differ, it is well known that the slower step is rate controlling, and that the over-all rate of the process can be no greater than that of the slower step. However, in a process involving several alternative steps to product, as in competition between cyclopolymerization ($M_1^{\cdot} \xrightarrow{k_c} M_c^{\cdot}$) and the usual intermolecular vinyl propagation of the <u>same monomer</u> ($M_1^{\cdot} + M \xrightarrow{k_{p_1}} M_c^{\cdot}$), an increase of k_c, the rate constant for the ring closure reaction, does not always result in an increase in the over-all rate. As shown below, the over-all rate depends also on the reactivity of the cyclic radical, $M_c^{\cdot}$.

Based upon Eqs. (1)-(8), Eq. (20) [6] can be used to define the over-all rate of cyclopolymerization, R_c.

$$R_c = (fk_d/k_t)^{1/2}[I]^{1/2}[M]\,\frac{k_{p_1}k_{p_2}[M] + k_{p_1}k_t(fk_d/k_t)^{1/2}[I]^{1/2} + k_{p_2}k_c}{k_c + \alpha k_{p_2}[M] + k_t(fk_d/k_t)^{1/2}[I]^{1/2}} \tag{20}$$

$$= \underline{\overline{K}}\,[I]^{1/2}[M]\,\frac{k_{p_1} + k_{p_2}k_c}{k_c + \alpha X} \tag{21}$$

where $\underline{\overline{K}} = (fk_d/k_t)^{1/2}$ and $X = k_{p_2}[M] + k_t(fk_d/k_t)^{1/2}[I]^{1/2}$.

The overall rate of the usual intermolecular vinyl propagation R_n, is obtained from Eq. (20) assuming $k_c = 0$, then,

$$R_n = k_{p_1}/\alpha(fk_d/k_t)^{1/2}[I]^{1/2}[M] \tag{22}$$

$$= k_{p_1}/\alpha\underline{\overline{K}}[I]^{1/2}[M] \tag{23}$$

Applying the assumption $R_c > R_n$, then

$$R_c - R_n > 0 \tag{24}$$

From Eqs. (2) and (4)

$$R_C - R_n = \underline{K}[I]^{1/2}[M]\left(\frac{k_{p1}X + k_{p2}k_C}{k_C + \alpha X} - \frac{k_{p1}}{\alpha}\right)$$

$$= \underline{K}[I]^{1/2}[M]\ \frac{(k_{p2} - k_{p1})k_C}{k_C + \alpha X} \qquad (25)$$

from Eq. (5)

$$k_{p2} - k_{p1}/\alpha > 0 \qquad (26)$$

$$\alpha \equiv k_{12}/k_{22} \quad \text{then} \quad k_{p2}/k_{p22} > k_{p1}/k_{p12} \qquad (27)$$

Assumption (24) corresponds to Eq. (27). If α is unity, Assumption (24) means that $k_{p22} \gg k_{p1}$. So Assumption (24) does not require that ring closure be faster.

If k_C is increased to βk_C ($\beta > 1$) and the over-all rate is R_C', the change of the rate is shown as follows from Eq. (20) or (21).

$$R_C' - R_C = \underline{K}[I]^{1/2}[M]\left[\frac{k_{p1}X + k_{p2}k_C\beta}{\beta k_C + \alpha X} - \frac{k_{p1}X + k_{p2}k_C}{k_C + \alpha X}\right]$$

$$= \underline{K}[I]^{1/2}[M]\ \frac{K_C X(\alpha k_{p2} - k_{p1})(\beta - 1)}{(\beta k_C + \alpha X)(k_C + \alpha X)} \qquad (28)$$

therefore,

$$\begin{aligned} R_C' - R_C &= 0 \longleftarrow \alpha k_{p2} = k_{p1} \\ &> 0 \longleftarrow \alpha k_{p2} > k_{p1} \\ &< 0 \longleftarrow \alpha k_{p2} < k_{p1} \end{aligned} \qquad (29)$$

Equation (29) shows that if α is unity, the over-all rate depends on k_{p2}, the reactivity of the cyclic radical. If only k_C is increased and $\alpha k_{p2} = k_{p1}$, then the rate is unchanged.

Consideration of the Cyclization Reaction As a Pseudo-Bimolecular Process

Although the rate constant, k_C, is a first-order rate constant, it can be expressed as a product of a second-order rate constant with a hypothetical concentration of the double bond of the same molecule as follows:

$$k_C \equiv k_p'[m] \tag{30}$$

where [m] means the speculative concentration of the double bond in the limited region surrounding the growing radical $M_i^{\cdot}$ which is based on the reaction rate, or, in other words, on the collision frequency. $k_p'[m]$ expresses the speculative state that the double bond is separated from the radical and undergoes collision with the radical in such a way that its concentration is [m].

As discussed earlier, the reactivity of $M_i^{\cdot}$ with a double bond of the same molecule may be similar to that of $M_C^{\cdot}$ with a double bond of another molecule unless conjugate groups of the cyclic radical is a component of the cyclized ring of $M_C^{\cdot}$. This assumption can be applied only to DCH (dicyanoheptadiene). Equation (30) can be rewritten as follows:

$$k_C = k_{p2}[m] \quad \text{or} \quad [m] = k_C/k_{p2} \tag{31}$$

However, k_C/k_{p2} cannot be obtained from the kinetics, but $\alpha k_{p2}/k_C$ can be obtained.

k_{11} and k_{22} are the bimolecular termination constants of $M_i^{\cdot}$ radical and $M_C^{\cdot}$ radical, respectively. Since the reactivity of $M_i^{\cdot}$ may be hindered sterically by the bulky substituent,

$$k_{11} \leqslant k_{22} \quad \text{or} \quad \alpha \equiv \sqrt{k_{11}/k_{22}} \leqslant 1 \tag{32}$$

should be expected. So Eq. (31) can be written as:

$$[m] \leqslant k_C/\alpha k_{p2} \tag{33}$$

The average distance between the radical $M_i^{\cdot}$ and the double bond on the same molecule, γ, is given by the following equation:

$$\frac{4\pi\gamma^3}{3} = \frac{1000 \times 10^{24}}{[m] \times 6.023 \times 10^{23}} \ (\text{A}^3) \tag{34}$$

Using the value of $\alpha k_{p2}/k_C$ of DCH in Table 4, [m] and γ of DCH can be calculated (Table 9).

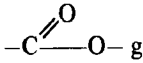
Table 9. Average Distance Between Radical and Double Bond of Dicyanoheptadiene

Temp (°C)	[m]	γ
40	$\leq$14.1	$\geq$3.04
50	$\leq$20.4	$\geq$2.69
60	$\leq$20.4	$\geq$2.69

In the case of MA, since the above first assumption cannot be made, then Eq. (31) cannot be applied so the average distance, γ, for this monomer is difficult to estimate.

From Table 9, it can be concluded that the average distance between the growing radical $M_i^{\cdot}$ and the double bond of the same molecule is greater than 3.0 Å at 40° or 2.7 Å at 50 or 60°C. The most probable distance of a five-linked chain has been given as 4.93 Å by Treloar [23]. Our concern is whether the distance, γ, is greater or less than 4.93 Å.

In order to discuss the details concerning the cyclization process, the termination constants of a series of monomers are necessary. However, these data in the series of α-alkyl acrylonitriles are not available. The data are available, however, in the series of alkyl methacrylates and acrylates. These are summarized in Table 10. In this series, the termination constant is decreased with an increase in the number of carbons of the alkyl group.

It appears reasonable to assume that the decrease of k_t with an increase in the number of carbons of the alkyl group in the α-alkyl acrylonitrile series may be much bigger than that in the methacrylate and acrylate series, because the decrease in over-all rate of the acrylonitrile series is much larger than the methacrylate series. The reason may be attributable to the contribution of the  $-C(=O)-O-$ group to the transition state of the propagation and the termination steps.

If the difference between the acrylonitrile series and the methacrylate or acrylate series can be neglected, the ratio, α, of DCH may be deduced from the ratio of n-propyl methacrylate (PMA) and MMA and so on, α values of these series are given approximately as follows:

$$\alpha\frac{\text{PMA}}{\text{MMA}} \doteqdot 0.9 \qquad \alpha\frac{\text{BMA}}{\text{MMA}} \doteqdot 0.4 \qquad \alpha\frac{\text{BA}}{\text{MA}} \doteqdot 0.09$$

Table 10. Summary of Propagation and Termination Constants for Alkyl Acrylates and Methacrylates

Monomer	Temp (°C)	k_p (1/mole sec)	k_t (1/mole sec)	Ref.
Methyl methacrylate (MMA)	22.5	384	44	24
	23.6	310	66	14
	25	512	45	25
	35.9	410	68	14
n-Propyl methacrylate (PMA)	30	467	45	26
n-Butyl methacrylate (BMA)	30	362	10	27
t-Butyl methacrylate (t-BMA)	25	350	14	28
Methyl acrylate (MA)	25	1500	55	29
	30	720	2.2	15
	60	2090	4.75	15
n-Butyl acrylate (BA)	25	13	0.018	30
	35	14.5	0.018	30

Using these values as the α-values for DCH, Eq. (4) and Table 1 can be rewritten as follows:

$$[m] = 0.9kc/\alpha kp_2 \qquad (4\text{-}1)$$

$$[m] = 0.4kc/\alpha kp_2 \qquad (4\text{-}2)$$

$$[m] = 0.09kc/\alpha kp_2 \qquad (4\text{-}3)$$

Table 11 shows the values of the average distance between reaction centers as estimated from Eqs. (4-1) to (4-3) are in the range of 2.8-6.8 Å, but a definite value cannot be determined from the above considerations alone.

Table 11. Estimated Distances Between Reaction Centers in DCH

α	Temp (°C)	[m]	γ
0.9	40	12.7	3.15
	50	18.4	2.78
	60	18.4	2.78
0.4	40	5.6	4.12
	50	8.2	3.65
	60	8.2	3.65
0.09	40	1.27	6.79
	50	1.84	6.00
	60	1.84	6.00

If the decrease of the termination constant of the α-alkyl acrylonitriles with increasing number of carbon atoms of the alkyl group is much bigger than that of acrylates; in other words, if α of DCH is smaller than α_{MA}^{BA}, the γ value of DCH should be larger than 6-6.8 Å. A value larger than 4.93 Å is not necessarily unreasonable, because of the dipole-dipole repulsion of the cyano groups. Even in this case, the cyclization step could be much faster than the propagation step on the $M_1^{\cdot}$ radical. This was an important conclusion in the earlier discussion and these results are not discrepant to that conclusion.

The hypothetical intramolecular double bond concentration of 20.4 M at 50° for 2,6-dicyano-1,6-heptadiene can only be interpreted that the reaction occurs much faster than would be predicted on the basis of the most probable distance of 4.93 Å as calculated by Treloar [23]. These concentration values compare favorably with the calculated value of 21.8 M for liquid ethylene at its boiling point, -102°. These observations can be interpreted most satisfactorily in terms of an essentially concerted reaction from attack on the diene by a radical species to formation of the cyclic radical. This interpretation is consistent with an earlier proposal [31] that a homoconjugative interaction between the double bonds of a 1,6-diene may account for the unique tendency of these unconjugated dienes to cyclopolymerize. These concepts have received further support based upon a spectroscopic study of a series of 1,6-dienes [32].

EXPERIMENTAL

Preparation of Monomers

Methacrylic Anhydride. Methacrylic anhydride was prepared using methacrylic acid and methacryloyl chloride [33]. The product was shown to be pure by vpc.

2,6-Dicyanoheptadiene-1,6 (DCH). Diethyl α,α′-Dicyanopimelate. In a 1-liter, three-necked flask equipped with a stirrer, a reflux condenser, and a dropping funnel, 11.5 g (0.5 mole) of sodium metal, 46 g of absolute ethanol, and 250 ml of tetrahydrofuran were heated at reflux temperature under anhydrous condition. After the sodium had dissolved, 283 g of ethyl cyanoacetate was poured into the solution. To the refluxing solution was added through a dropping funnel 50.5 g of 1,3-dibromopropane over a 3-hr period, and refluxing was continued for an additional hour. The THF was then evaporated from the mixture. After cooling the residue with ice water, 500 ml of benzene and 200 ml of water saturated with sodium sulfate were added. The benzene solution was collected and washed with 200 ml of saturated sodium sulfate and twice with 250 ml of water containing 5 ml of sulfuric acid, and then with 200 ml of saturated sodium sulfate. The benzene and excess ethyl cyanoacetate were evaporated from the solution under diminished pressure. The residue was 39.5 g of slightly yellow liquid. After distillation of the product, 37 g (55% yield) of pure diethyldicyanopimelate, bp 182-185°C/0.05 mm Hg was obtained, which showed only one peak on vpc. IR spectrum: 2230 cm^{-1} (C–N), 1750 cm^{-1} (–CO_2R). n_d^{21} = 1.4546. Analysis calculated for $C_{13}H_{18}O_4N_2$; C, 58.7; H, 6.77; N, 10.52. Found: C, 58.62; H, 7.03; N, 10.44.

2,6-Dicyanoheptadiene-1,6. Potassium hydroxide, 26 g, was dissolved in 900 ml of absolute ethanol and 62 g of diethyl dicyanopimelate was added. The solution was stirred at room temperature for 24 hr under anhydrous condition. The ethanol was then removed under diminished pressure at room temperature. The residue was dissolved in 400 ml of water, washed with ether, acidified by addition of 50% hydrochloric acid, and extracted with ether. The ether solution was dried over anhydrous sodium sulfate. After removal of ether, 103.2 g of crude α,α′-dicyanopimelic acid, mp 120°C, decomposition point 175°C, was obtained. 103.2 g of α,α-dicyanopimelic acid was dissolved in 196 g of a 25% aqueous solution of dimethylamine with cooling in an ice bath after which 160 g of 37% solution of formaldehyde was added. The mixture was gently refluxed for 24 hr. The oily layer was separated from the reaction mixture and the aqueous layer was washed with 100 ml of ether. The oily layer and the ether extract were combined and distilled in the presence of a small amount of 2,6-di-tert-butyl-p-cresol. 63.4 g of DCH was obtained, bp 92°C (0.06 mm Hg), n_d^{21} = 1.4690. The IR spectrum showed nitrile (2220 cm^{-1}) and terminal methylene (3100, 1860, 1625, 1140, and 943 cm^{-1}) groups. The UV spectrum showed λ_{max}199 mμ,ϵ_{max} 20,600. (Beckman DK-2 spectrophotometer, in acetonitrile). Literature reports [34] λ_{max} 200 mμ, ϵ_{max} 15,900 (in EtOH). Analysis Calculated for $C_9H_{10}N_2$: C, 73.94; H, 6.90; N, 19.16. Found: C, 73.92; H, 7.05; N, 19.09. The product was shown to be pure by vpc.

2-Cyanoheptene-1. Ethyl α-Cyanoheptylate. Ethyl α-cyanoheptylate was prepared by a procedure similar to that used for diethyl α,α′-dicyanopimelate, using ethyl cyanoacetate and 1-bromopentane. From 151 g (1 mole) of 1-bromopentane, 131.5 g (0.72 mole) of ethyl cyanoheptylate, bp 97°C/0.7 mm Hg, was obtained. It was shown to be pure by vpc.

2-Cyanoheptene-1. The procedure used for preparation of 2-cyanoheptene-1 was the same as that described above for 2,6-dicyanoheptadiene-1,6. From 131.5 g of ethyl α-cyanoheptylate, 57.0 g (0.47 mole) of 2-cyanoheptene-1, bp 60-63°C/5 mm Hg, n_d^{26} = 1.4281, was obtained. The IR spectrum showed nitrile (2220 cm^{-1}) and terminal methylene (3110, 1870, 1620, and 930 cm^{-1}) groups. The product was pure on vpc.

2,6-Diphenylheptadiene-1,6 (DPH). DPH was prepared according to Field [35]. The compound was shown to be pure by vpc.

2-Phenylheptene-1. The procedure was same as Field's [35]. The product, bp 78-83°C/0.75 mm Hg, n_d^{26} = 1.5099, was obtained in 87% yield from benzoyl pentane. Analysis Calculated for $C_{13}H_{18}$: C, 89.66; H, 10.34. Found: C, 89.79; H, 10.52. The compound was shown to be pure by vpc.

Methacrylic Isobutyric Anhydride (MIA). Methacrylic isobutyric anhydride was at first prepared from sodium methacrylate and isobutyryl chloride according to Hwa [36]. The colorless product was obtained in 88% yield. It was carefully fractionated by use of a spinning band column, and three fractions, bp 29-30°C/0.25 mm Hg, bp 30°C/0.25 mm Hg, and bp 31°C/0.25 mm Hg, were obtained.

1st fraction. n_d^{24} = 1.4100, IR spectrum of the anhydride group appeared at 1749 and 1814 cm^{-1}. This coincided with isobutyric anhydride: n_d^{24} = 1.4050; IR: 1749, 1814 cm^{-1}.

2nd fraction. n_d^{24} = 1.4235; IR spectrum: 1731 (with a shoulder at 1745 cm^{-1}), 1805 cm^{-1}.

3rd fraction. n_d^{24} = 1.4440, IR spectrum: 1728, 1785 cm^{-1} (1805 cm^{-1} shoulder). This fraction was similar to methacrylic anhydride: n_d^{24} = 1.4534; IR spectrum, 1723, 1784 cm^{-1}.

Since the IR spectrum of the 2nd fraction was different from either methacrylic anhydride or isobutyric anhydride, it was assumed to be isobutyric methacrylic anhydride. Grey [37] has reported that a 1:1 M mixture of the two anhydrides showed four peaks in the region of anhydride. However, the NMR spectrum of the second fraction showed two hydrogens for terminal double bond at 3.87 and 4.22-4.24 τ, while the spectrum of MA showed them at 3.84 and 4.21 τ. The differences were too small to evaluate. The spectrum of methacrylic isobutyric imide appears at 4.00 and 4.36 τ, while that for methacrylic imide appears at 4.11 and 4.30 τ [38]. The differences are 0.11 and 0.06 τ. Accordingly, the above 2nd fraction appears to be a mixture of two or three anhydrides. Their separation was unsuccessful.

The method of preparation of the anhydride by Yakuborich [33] was also used, but the products were similar to the above products.

Purification of Other Materials

DMF was purified according to Smets [1]. AIBN was recrystallized twice from toluene keeping the temperature below 40°C.

Determination of Over-all Rate of Polymerization

The over-all rate of polymerization of MA and DCH was determined by dilatometry. For the thermostat, a Sargent Thermonitor was used, which was capable of maintaining ±0.015°C of accuracy at 80°C. A Gaertner's cathetometer having a smallest scale reading of 0.01 mm was used for the measurement of contraction of the polymerization mixture. The dilatometer had about 9 ml capacity and the diameter of the capillary was 1 mm. Every determination was carried out to less than 10% conversion of the monomers.

The rates of CH, DPH, PH, and α-methyl styrene were determined by gravinometry. The mixtures of AIBN solvent and monomer were put into glass tubes from which the air was removed under high vacuum with cooling in a Dry Ice-acetone bath and which were then warmed to room temperature. The procedure was repeated three times, after which the tubes were sealed under high vacuum. After polymerization, the mixture of DPH was poured into methanol, and PDPH was obtained as the precipitate. PCH and PPH were obtained after the solvents and the monomers were removed under vacuum at room temperature from the polymerization mixtures. The resulting viscous liquids were dried under vacuum at 50°C for 24 hr and weighed. Weights of the polymers were calculated after correction for the weight of AIBN. Only AIBN was obtained from the polymerization of α-methyl styrene.

Determination of Over-all Rate of Polymerization

Determination of the residual unsaturation of PDCH, which was obtained from the polymerization mixture by precipitation in methanol, was carried out as follows: 70 mg of PDCH ([D] = 4.5, at 40, 50, and 60° in Table 2) was dissolved in 1 g of deuterated dimethyl sulfoxide. The NMR spectra of the solutions were obtained at room temperature using Varian-60. No peak was observed in the region of unsaturation between 4.0 and 4.3 τ, while a broad peak was observed at 7.0-9.0 τ, of intensity about 80. The ratio of sp^2 to sp^3 hydrogen was assumed to be less than 0.5/80. k_{pi}/k_c values were calculated from these results.

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