Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

The Fundamental Basis for Cyclopolymerization. X. A Systematic Study of the Cyclopolymerization of Methacrylic Anhydride

T. Flint Gray Jr.[a]; George B. Butler[a]
[a] Center for Macromolecular Science and Department of Chemistry, University of Florida, Gainesville, Florida

To cite this Article Gray Jr., T. Flint and Butler, George B.(1975) 'The Fundamental Basis for Cyclopolymerization. X. A Systematic Study of the Cyclopolymerization of Methacrylic Anhydride', Journal of Macromolecular Science, Part A, 9: 1, 45 — 82

To link to this Article: DOI: 10.1080/00222337508068646

URL: http://dx.doi.org/10.1080/00222337508068646

J. MACROMOL. SCI.—CHEM., A9(1), pp. 45-82 (1975)

The Fundamental Basis for Cyclopolymerization. X. A Systematic Study of the Cyclopolymerization of Methacrylic Anhydride*

T. FLINT GRAY, Jr. and GEORGE B. BUTLER

Center for Macromolecular Science and
Department of Chemistry
University of Florida
Gainesville, Florida 32611

ABSTRACT

The study of methacrylic anhydride has shown that the intramolecular propagation step has a higher energy of activation (2.6 ± 0.3 kcal/mole) than the intermolecular step. Steric factors have, however, been found to favor cyclization (A_{11}/A_c = 0.0039 liter/mole). It has been concluded that the conditions which favor cyclization in methacrylic anhydride are high temperature, low monomer concentration, poor solvent system, and high conversion. The increase in cyclization caused by heterogeneous conditions, such as poor solvent or high conversion, appears to be due to tight coiling of the polymer chain and slow diffusion, thereby decreasing the value of k_{11} with respect to k_c. Although methacrylic anhydride

---

*Taken from the Ph.D. Dissertation of T. Flint Gray, Jr., University of Florida, December 1964.

does cross-link to some extent, the number of cross-links was lower than expected due to anhydride interchange of pendent units. Also, even though some cross-links were present, the polymer could be dissolved due to interchange of the intermolecular cross-links to intramolecular anhydride units. The bathochromic shift observed for methacrylic anhydride, when its UV spectrum was compared with those for the methacrylate esters, was found to result from added electronic stabilization of the α,β-unsaturated system through resonance of the nonbonded electrons on the acyl oxygen with the carbonyl unit attached to it. In a stereochemical configuration study on methacrylic anhydride, no solvent effect could be found. The influence of increasing temperature and conversion was found to be small, but appeared to increase the heterotacticity and decrease the syndiotacticity by equivalent amounts. Noncyclic anhydride units resulted in increased syndiotactic character. The tacticities observed were explained on the grounds of a random cyclic propagation step and a stereospecific intermolecular step. The results of the model study on methacrylic anhydride have been combined with the literature pertinent to the mechanism and stereochemistry of cyclopolymerization in order to develop a general understanding of these areas. After thorough consideration, it seems that the driving-force for cyclization in cyclopolymerizations is due to: 1) statistical probability, 2) thermodynamic stability, and 3) steric and entropy effects. In many dienes, nonconjugated excited state interactions are also very important. The driving force for the higher degrees of polymerization, observed in cyclopolymerization for difficultly polymerizable systems, may be due to steric factors. Stereochemical studies have shown that the high degrees of order which are observed in cyclopolymerization are due to the cyclic units that are formed. It also appears that free radical cyclopolymerizations yield the kinetically controlled product while the alkyl-metal coordination catalysts give the thermodynamic product.

INTRODUCTION

As was pointed out in the previous paper in this series [1], certain aspects of the cyclopolymerization mechanism remain to be justified in terms of experimental observations. It was the purpose of this invertigation to undertake a thorough mechanistic and stereochemical study of a suitable model monomer capable of cyclopolymerization in an effort to clarify these remaining aspects. Methacrylic anhydride was chosen as the model because it fit the qualifications of: 1) availability, 2) a conjugated system which lends itself to an ultraviolet spectral study, 3) the presence of a hydrolyzable group useful in studying the fraction of noncyclic units, and 4) allowing stereochemical configuration to be determined.

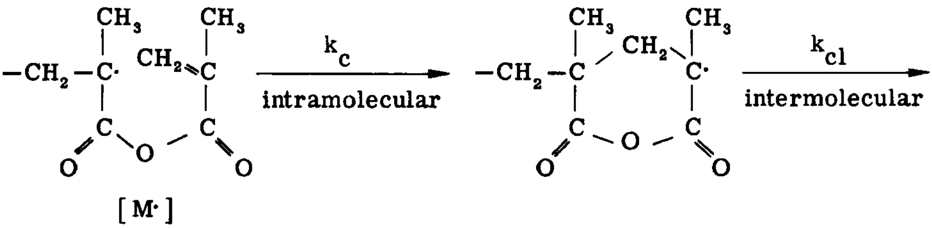
RESULTS AND DISCUSSION

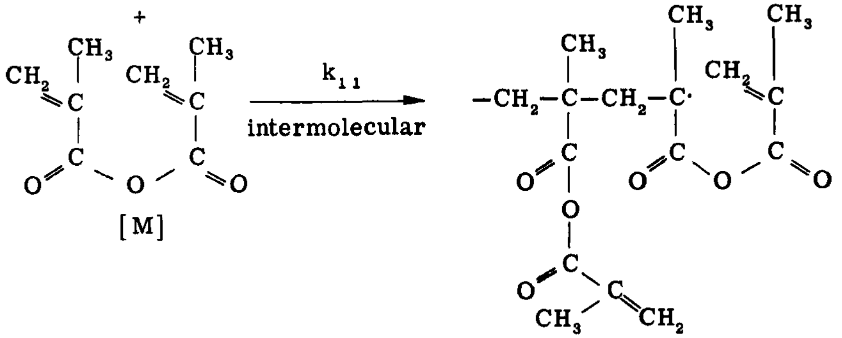
Kinetics

In cyclopolymerization, diene units which fail to cyclize leave pendent double bonds unless subsequently involved in cross-linking. The number of these pendent units permits calculation of the number of cyclic units for a given amount of polymer. The number of noncyclic methacrylic anhydride units could easily be determined by bromimetric titration for the methacrylic acid produced when a sample of poly(methacrylic anhydride) was hydrolyzed. Knowledge of the number of noncyclic units can be treated as a function of concentration and temperature. Combining the data obtained in these studies with kinetic equations similar to those used by Mercier and Smets [2], the important relationships of the ratio of rates and the difference in energy for intramolecular and intermolecular propagations may be obtained.

In order for the kinetic equations to be valid, two conditions must be met. First, monomer concentration must be assumed to be the same before and after polymerization. Second, any unit which fails to cyclize must not enter another polymer chain. For these approximations to be valid, the conversion of monomer to polymer must be as low as possible. Experimentally it was found that conversions of 0 to 4% were satisfactory.

The kinetic relationship between intramolecular and intermolecular propagation can be derived from the following reaction scheme:





The rate of intermolecular propagation (R_{11}) is given by:

$$R_{11} = k_{11}[M\cdot]\,(2[M]) \tag{1}$$

(where [M] is given in moles of diene and therefore must be doubled to account for all double bonds present) and similarly for the intramolecular propagation rate (R_c):

$$R_c = k_c[M\cdot] \tag{2}$$

The ratio of R_{11} to R_c results in the expression:

$$R_{11}/R_c = 2k_{11}[M]/k_c \tag{3}$$

The relationship which relates the experimentally determined fraction of cyclic units (f_c) to the rates R_{11} and R_c is

$$f_c = \frac{R_c}{R_{11} + R_c} \tag{4a}$$

or

$$\frac{1}{f_c} = 1 + \frac{R_{11}}{R_c} \tag{4b}$$

which, on substitution of Eq. (3) for R_{11}/R_c, gives

$$\frac{1}{f_c} = 1 + \frac{2k_{11}[M]}{k_c} \qquad (5)$$

A plot of $1/f_c$ vs $[M]$ results in a straight line with an intercept at infinite dilution corresponding to complete cyclization and a slope with a value of $(2k_{11}/k_c)$.

The experimentally determined values of $1/f_c$ as a function of concentration of methacrylic anhydride in dimethylformamide are given in Table 1. A plot of $1/f_c$ vs $[M]$ (Fig. 1) results in a slope with a value of 0.83 liter/mole; therefore, at 0°C the ratio of k_{11}/k_c = 0.42 liter/mole. Table 2 and Figs. 2 and 3 give the values of k_{11}/k_c at various temperatures in the range -20 to +80°.

By substitution of the Arrhenius equation into Eq. (3), a relation is obtained which allows the calculation of the energy difference between an intramolecular and an intermolecular propagation step. It must be assumed, however, that the degrees of polymerization are high enough that the differences in possible termination steps are negligible.

$$R_{11}/R_c = 2k_{11}[M]/k_c \qquad (3)$$

TABLE 1. Cyclization of Methacrylic Anhydride as a Function of Concentration[a]

[M] (moles/liter)	f_c	$1/f_c$
6.0	0.16	6.3
4.0	0.25	4.0
3.25	0.26	3.8
2.0	0.35	2.9
1.0	0.55	1.8

[a] Solvent, dimethylformamide; [benzoin]: 0.25 wt% based on methacrylic anhydride; temperature, 0.0°C.

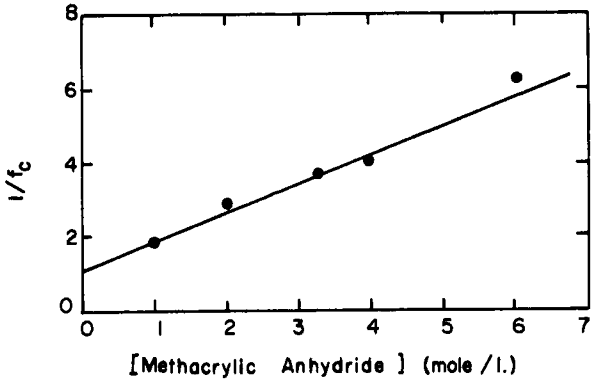


FIG. 1. Variation of $1/f_c$ as a function of methacrylic anhydride concentration in dimethylformamide Slope = 0.83 liter/mole.

$$\frac{R_{11}}{R_c} = (2/M])\frac{A_{11}e^{-E_{11}/RT}}{A_c e^{-E_c/RT}} \tag{6a}$$

$$\log_{10}\frac{R_{11}}{R_c} = \log_{10}(2[M])\frac{A_{11}}{A_c} + \frac{E_c - E_{11}}{2.303RT} \tag{6b}$$

The difference in energy ($E_c - E_{11}$) can be calculated from the slope of a plot of $\log_{10} R_{11}/R_c$ vs 1000/T for a constant monomer concentration.

The experimental results of the variation of cyclic units as a function of temperature for the polymerization of methacrylic anhydride at a concentration of 3.25 moles/liter in dimethylformamide are listed in Table 3. The value of the slope of a plot of $\log_{10} R_{11}/R_c$ against 1000/T (Fig. 4) was found to be 0.563, which corresponds to an energy difference ($E_c - E_{11}$) of 2.6 ± 0.3 kcal/mole. The value of the ratio A_{11}/A_c was found to be 0.0039 liter/mole.

The results of the kinetic study indicate that the intramolecular propagation step requires 2.6 ± 0.3 kcal/mole greater energy than the intermolecular step. It is, however, noted that the rate of cyclization is considerably larger than that for intermolecular propagation.

TABLE 2. Variation of k_{11}/k_c as a Function of Temperature[a]

Temperature (°C)	f_c	$1/f_c$	k_{11}/f_c
80.0	0.51	2.0	0.16
50.0	0.47	2.1	0.17
35.0	0.38	2.6	0.25
20.0	0.33	3.0	0.31
0.0	0.26	3.8	0.43
-10.0	0.23	4.3	0.50
-20.0	0.20	5.0	0.62

[a] Solvent, dimethylformamide; [benzoin], 0.25 wt% based on methacrylic anhydride; [methacrylic anhydride], 3.25 mole/liter.

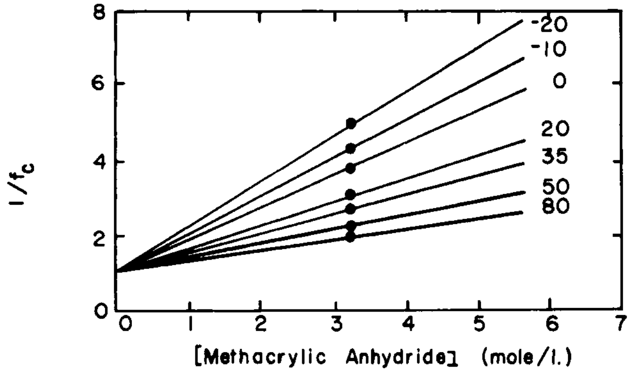


FIG. 2. Variation of $1/f_c$ as a function of methacrylic anhydride concentration in dimethylformamide at various temperatures (°C).

Furthermore, from the Arrhenius treatment the value of the ratio A_{11}/A_c indicates a very high steric factor favoring cyclization.

During the pursuit of a similar kinetic study, Gibbs and Murray [3] obtained results which indicated that the rate of propagation of methacrylic anhydride is dependent on the 3/2 power of monomer concentration. Since methyl methacrylate exhibits ideal behavior in

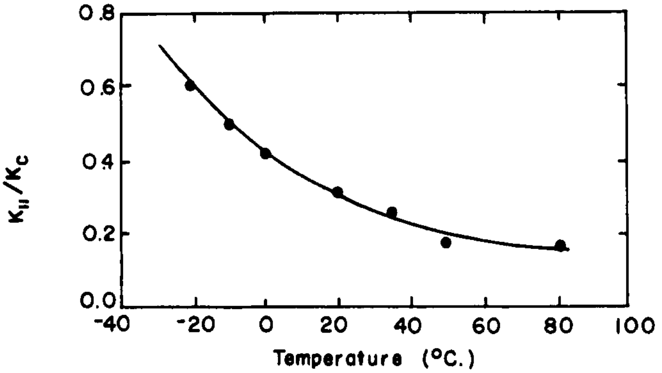


FIG. 3. Variation of k_{11}/k_c as a function of temperature for methacrylic anhydride in dimethylformamide.

TABLE 3. Cyclization of Methacrylic Anhydride as a Function of Temperature[a]

Temperature (°C)	$\frac{1000}{T\ (°K)}$	f_c	R_{11}/R_c	$\log_{10}\frac{R_{11}}{R_c}$
80.0	2.84	0.51	0.96	-0.0177
50.0	3.10	0.47	1.13	0.0531
20.0	3.42	0.33	2.03	0.3075
0.0	3.67	0.26	2.85	0.4548
-10.0	3.80	0.23	3.35	0.5250
-20.0	3.96	0.20	4.00	0.6021

[a] Solvent, dimethylformamide; [benzoin], 0.25 wt% based on methacrylic anhydride; [methacrylic anhydride], 3.25 mole/liter.

azobisisobutyronitrile-initiated polymerizations, it was expected that the rate for methacrylic anhydride would also show first-power dependence on monomer concentration. It was suggested that the 3/2 power dependency was due to low efficiency of initiation. In the light of the results of this study on the fraction of cyclic units at various concentrations and temperatures, it appears that another explanation is possible, based on the fact that even at low concentrations, such as

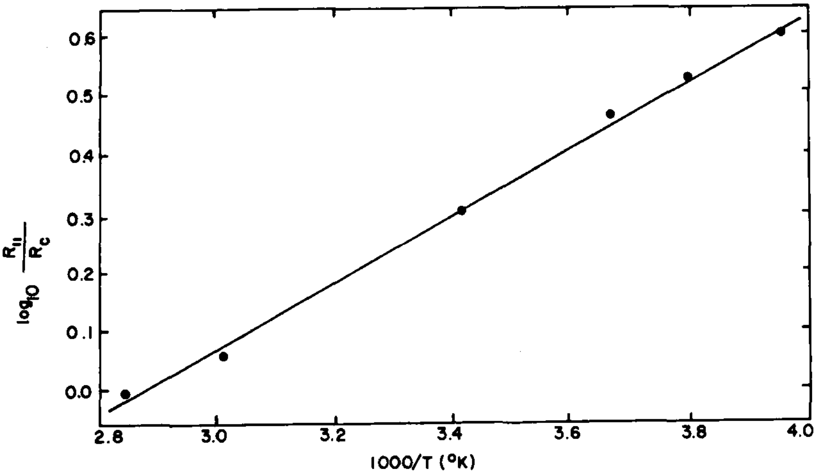


FIG. 4. Arrhenius plot of $\log_{10} R_{11}/R_c$ as a function of 1000/T.

Gibbs and Murray used, there are still small numbers of noncyclic anhydride units present. Since the rate of polymerization was found by isolation of polymer over various time intervals, the rate will be correct in terms of moles of monomer which disappear; however, it will not be correct with respect to the number of double bonds which have reacted. In order to be a true measure of the rate of cyclopolymerization, the rate Gibbs and Murray observed must be corrected for those double bonds which did not enter the polymer chain. By using the following equations, the rate data of Gibbs and Murray [3] and the fraction of cyclization obtained in this work, the rate of propagation can be corrected. The corrected rate values (R_p') are listed in Table 4.

$$f_r = f_c + 1/f_n \tag{7}$$

where f_r = fraction of double bond reacted.

f_c = fraction of cyclic units, monomer enters chain through both double bonds.

f_n = fraction of noncyclic units, monomer enters chain through one double bond.

$$R_p' = f_r R_p \tag{8}$$

TABLE 4. Rate of Propagation of Methacrylic Anhydride Corrected for Fraction of Noncyclic Units

$[M]^a$ (mole/liter)	$R_p{}^a$	$f_c{}^b$	f_r	R_p'
0.72	9.5	0.73	0.87	8.35
0.49	5.8	0.80	0.90	5.20
0.35	3.6	0.85	0.93	3.35
0.14	1.7	0.94	0.97	1.65
0.074	0.9	0.98	0.99	0.89

[a] Data from Ref. 3. Solvent, dimethylformamide; temperature, 40°C.

[b] Data from results here. Solvent, dimethylformamide; temperature, 40°C.

where R_p = moles of monomer disappearing per unit time.

R_p' = moles of monomer, corrected for noncyclic units, disappearing per unit time.

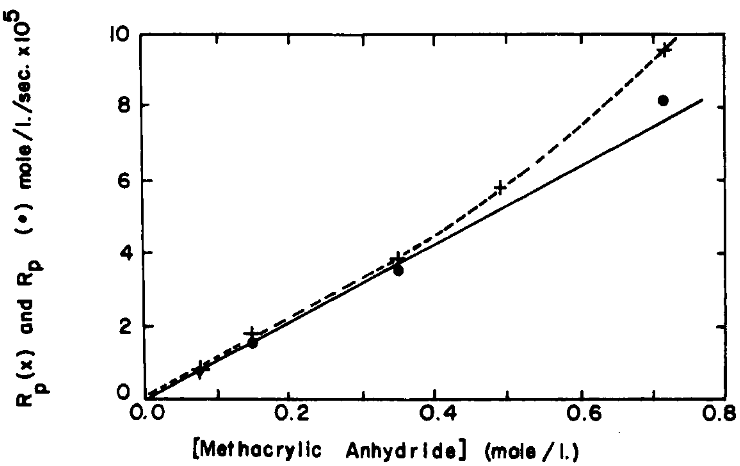


FIG. 5. Rate of propagation of methacrylic anhydride corrected for the fraction of noncyclic units. (-•-) Corrected and (-x-) Gibbs.

The plot of R_p' versus monomer concentration shows that the corrected rate is proportional to the first power of monomer concentration (Fig. 5). It appears, therefore, that there is nothing unusual in the dependence of rate on monomer concentration at the low concentrations used.

Gibbs and Murray [3] found the energy of activiation for methacrylic anhydride ($E_p - E_t/2$) to be 8.0 kcal/mole. A comparison was made with $E_p - E_t/2$ for methacrylic acid which was found to be 9.8 kcal/mole. It was concluded from this comparison of activation energies that there is little, if any, difference between normal vinyl polymerization energetics and those for cyclopolymerization of methacrylic anhydride. The results obtained in this work, however, show that the intramolecular propagation step requires 2.6 ± 0.3 kcal/mole more energy than the intermolecular step. With this additional information coupled with the fact that copolymerization studies have shown that the noncyclic and cyclic methacrylic anhydride radicals have equivalent reactivity [4], it would appear that a comparison between methyl methacrylate and methacrylic anhydride would be more reasonable since $E_p - E_t/2$ equals 5.0 kcal/mole for methyl methacrylate [5]. Addition of the energy increment necessary for an intramolecular propagation step would give a value of 7.6 kcal/mole, quite close to the value determined experimentally. The difference between inter-intermolecular and intra-intermolecular polymerization would be readily apparent from the latter comparison.

A second piece of data, which initially appeared to contradict the kinetic results gathered here, centered around the interpretation Hwa, Fleming, and Miller [6] had given volume shrinkage results. It was found that the polymerization of methacrylic anhydride resulted in a volume shrinkage of only 13.7 ml/mole of unsaturation compared to 22 to 23 ml/mole observed for methyl, ethyl, and propyl methacrylates. The low volume shrinkage was interpreted to indicate a preorientation of the methacrylic anhydride in a cyclic conformation, thus requiring little volume change on polymerization. The preorientation was also suggested to be the driving force for cyclization in the intra-intermolecular polymerization of methacrylic anhydride. However, it has since been shown that the volume shrinkage of phenyl benzyl and cyclohexyl methacrylates are all very close to 15 ml/mole [7]. In the light of these data, it would appear that the low volume shrinkage observed for methacrylic anhydride may be a characteristic of polymerization systems containing cyclic units in or near the polymer chain.

Solvent Effects

As has been discussed, the fraction of cyclic units in methacrylic anhydride polymer is dependent on both temperature and concentration. In addition it was observed that solvent plays a role in the determination

TABLE 5. Solvent Influence on Intra-Intermolecular Polymerization of Methacrylic Anhydride[a]

Benzene		Cyclohexanone		Dimethylformamide	
Conversion (%)	f_c	Conversion (%)	f_c	Conversion (%)	f_c
0.6	0.18	1.2	0.36	2.1	0.26
2.3	0.26	2.6	0.38	3.9	0.25
3.2	0.33	3.2	0.36	4.3	0.29

[a] Temperature, 0.0°C.; [benzoin], 0.25 wt% based on methacrylic anhydride; [methacrylic anhydride], 3.25 mole/liter.

of the amount of cyclization. From Table 5, two interesting points are observed. First, while conversion between 0 to 4% does not appear to influence cyclization in cyclohexanone and dimethylformamide, the fraction of cyclic units continually increases in benzene. Second, it is noted that cyclohexanone appears to give substantially higher cyclization than dimethylformamide.

Comparison of the value for k_{11}/k_c (0.25 liter/mole at 35°C) obtained in dimethylformamide with that reported by Smets, Hous, and Deval [8] for polymerization in cyclohexanone (0.022 liter/mole at 36.6°C) shows that the rate of cyclization is much larger in the latter solvent, thus adding proof to the reality of the solvent effect. It must be noted, however, that the magnitude of the solvent effect may not be as large as the difference in value of k_{11}/k_c indicate. The reason for this apparent discrepancy is that the above authors [8] carried conversion as high as 10% in their study of the fraction of cyclic units as a function of concentration. In the research for this paper, it was found that conversions above 5%, when the methacrylic anhydride concentration was greater than 2 moles/liter, invariably lead to higher values for the fraction of cyclic units than obtained in the 0 to 4% range. Further indication that the magnitude of the value may be in error is given in a comparison of k_{11}/k_c for methacrylic anhydride in cyclohexanone obtained here and that reported by Mercier and Smets [2] for acrylic anhydride under identical conditions. This comparison (Fig. 6) shows that at 0°C, both monomers have approximately the same value of k_{11}/k_c. Smets, Hous, and Deval [8] make a similar comparison and find that the value for k_{11}/k_c is 0.022 liter/mole at 36.6°C for methacrylic anhydride while acrylic anhydride has a value of 0.17 liter/mole at 35°C. Though the relative difference between k_{11}/k_c values

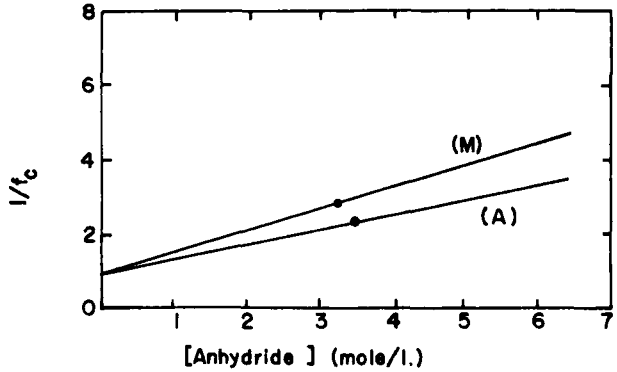


FIG. 6. Variation of $1/f_c$ as a function of anhydride concentration in cyclohexanone at 0°C (k_{11}/k_c: 0.26 for methacrylic anhydride; 0.20 for acrylic anhydride). (M) = Methacrylic anhydride and (A) = acrylic anhydride.

for methacrylic and acrylic anhydrides may change with temperature, it is not probable that the large change observed above will occur over a 35°C range. However, even though there may be some question of the actual magnitude of the solvent effect in going from cyclohexanone to dimethylformamide, the direction of the results is the same in both sets of data.

Having established the presence of a solvent effect in the cyclopolymerization of methacrylic anhydride, it is necessary to give a reasonable explanation for its occurrence. In approaching this problem it is immediately recognized that in some manner the solvent must influence the magnitude of k_{11} relative to k_c. On examination of the data, it is noted that poly(methacrylic anhydride) is insoluble in both cyclohexone and benzene, but soluble in dimethylformamide. This tends to indicate that precipitation of the growing polymer chain favors cyclization. The reason cyclization may be enhanced by precipitation is that the lower the solvation of a polymer chain, the tighter it will coil [9]. By being both heterogeneous with respect to monomer and solvent and tightly coiled, it seems logical that the radical would be sterically hindered to such an extent that very exacting orientation of incoming monomer molecules would be necessary for reaction to occur. Due to this increased orientation requirement and slower diffusion of monomer in the heterogeneous medium, k_c would become more and more favorable with respect to k_{11} as the system becomes increasingly heterogeneous [10].

The fact that a system such as methacrylic anhydride in benzene or cyclohexanone could be heterogeneous enough at low conversion to cause increased coiling and thereby favor k_c is substantiated by research with both acrylic and methacrylic anhydride. Acrylic anhydride polymerized in cyclohexanone has been found to exhibit kinetics typical of a heterogeneous system at low concentrations and conversions. Also, a tremendous rise in the heterogeneous nature of the system was observed by light scattering at conversions lower than 2% [11]. In addition it has been found that the rates of polymerization, even at low concentrations, for acrylic [11] and methacrylic [3, 8] anhydrides are much faster in cyclohexanone than in dimethylformamide. This is probably due to the early operation of the Trommsdorff effect resulting from the heterogeneous cyclohexanone system.

Added weight for the argument that the rate of cyclization may be favored by precipitation is obtained from the kinetic data obtained in the heterogeneous polymerization of methyl methacrylate [12]. It was shown in this study that although the overall rate of polymerization increased over the first few percent conversion, the value of k_p continually decreased (Table 6). The decrease in the size of k_p shows that the bimolecular reaction is slowed considerably due to the heterogeneous medium. The implication for cyclopolymerization is that heterogeneous conditions lead to a marked decrease in k_{11}, and probably influence k_c to only a small extent since it is a unimolecular reaction, thus resulting in a higher value for k_c/k_{11} which is observed as a higher fraction of cyclization.

Conversion Effects

In expanding the study of cyclopolymerization of methacrylic anhydride, it was noted that polymers obtained from conversion of 30 to 80% (prepared from equal weights of monomer and benzene, cyclohexanone, or dimethylformamide, using UV light and 0.25 wt% of benzoin, and a temperature range of -60 to +100°C) always gave values for the fraction of cyclization between 0.85 and 0.95 (see Table 12). In comparing these results with those obtained at low conversion (Table 2) under similar conditions (3.25 mole/liter and a temperature range of -20 to +80°C), it is obvious that the value of f_c has increased tremendously from low to high conversion. The explanation for this apparent increase in cyclization is difficult and may involve as many as four factors.

First, it is quite obvious that increasing conversion favors cyclization due to depletion of available monomer. This, however, does not

TABLE 6. Dependence of Rate and Velocity Coefficients on the Extent of Reaction for the Heterogeneous Polymerization of Methyl Methacrylate in 50% Cyclohexane Solution at 22.5°C [12]

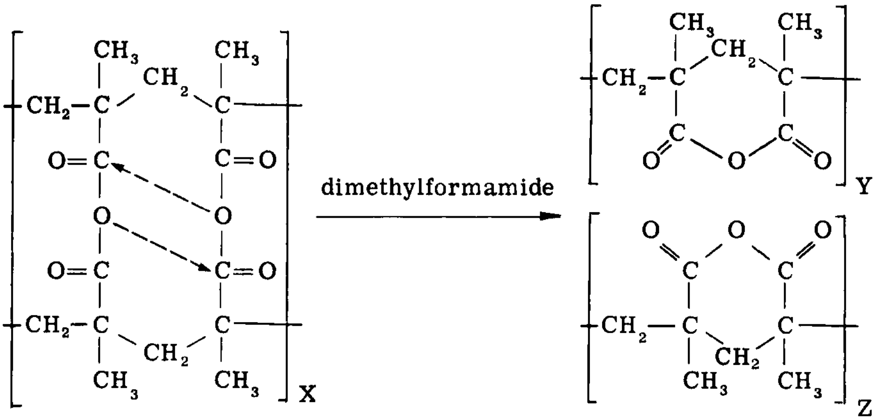
Conversion (%)	Rate (%/hr)	k_p [liter/(mole)(sec)]	k_t [liter/(mole)(sec)]
0	1.69	167	3.54×10^7
1	1.91	133	1.78×10^7
2	2.31	134	1.25×10^7
3	3.13	76	2.16×10^6
4	4.46	61	6.84×10^5
5	5.22	44	2.67×10^5
6	5.36	30	1.18×10^5
12	3.3	-	-

account for the complete difference in the fraction of cyclization observed, but does explain a part of it.

Second, some of the unsaturation present at low conversion probably disappears at higher conversion due to cross-linking reactions. This factor has been established [3] in a study of intrinsic viscosity as a function of conversion at various methacrylic anhydride concentrations. Evidence was obtained for gel formation at all conversions if the methacrylic anhydride concentration was greater than 34% by weight. Below this concentration the conversion could be taken to at least 20% before gel appeared. At conversions higher than 20 to 30% it would seem that the poly(methacrylic anhydride) would become totally insoluble. It was observed, however, that all samples would dissolve in dimethylformamide to give at least a 1% solution. The time necessary for complete solution to occur was generally 1 to 2 days. This time period required to dissolve poly(methacrylic anhydride) may be either a characteristic of the polymer due to its molecular weight and rigidity or the result of a slow catalytic effect of dimethylformamide which breaks intermolecular cross-links.

The possibility that the time for solution is characteristic of poly(methacrylic anhydride) seems reasonable since it was found here that the poly(methyl methacrylate) prepared from poly(methacrylic anhydride) had a viscosity-average molecular weight of 200,000 to 350,000 when benzene and dimethylformamide were the polymerization solvents and 50,000 to 100,000 when cyclohexanone was present. The molecular weight added to the known rigidity of the methacrylic anhydride polymer chain could easily result in difficult solubility. Also adding weight to this argument is the fact that repeatedly dissolving and isolating the polymer does not substantially change its IR spectrum or the time required for it to dissolve.

Since it has been shown [3] that above a concentration of 34% some gel is present at all conversions, there must be at least a few cross-links present in the polymers studied here. Therefore, in order for these polymers to dissolve, at least some of the cross-links must be broken. This would probably be a time-consuming process which may be the reason for the time required for poly(methacrylic anhydride) to dissolve. This process may be illustrated as follows:



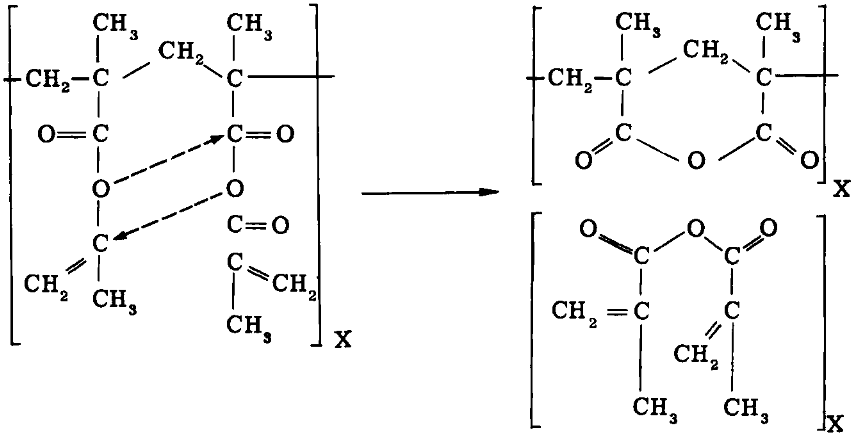
It was found that only 6 to 12 hr are required to dissolve polymers obtained from polymerization of methacrylic anhydride at a concentration of 0.2 mole/liter. This seems to support the possibility of some type of catalytic effect. Other authors [6, 13] have also noted the possibility of this catalytic effect. It was found that while methacrylic anhydride gives soluble polymer, many copolymers of methacrylic anhydride are highly insoluble, indicating that noncyclic anhydride units when flanked by a different monomer cannot undergo the interchange illustrated above.

In brief, it appears that cross-linking may account for some of the apparent increase in cyclization with conversion, but the exact extent that can be attributed to cross-linking becomes clouded due to the difficulty in interpreting solubility data. In this connection, however, it may be noted [10] that pendent double bonds do not cross-link as readily as might be imagined due to the necessity of two bulky chains diffusing together; thus the number of cross-links which may result from the high number of noncyclic units at low conversion is probably much less than the difference in the apparent value of cyclization indicates.

Third, perhaps one of the more important reasons for increased cyclization at high conversion is due to precipitation of the polymer chain.

Even when dimethylformamide is used as a solvent, precipitation occurs since, at conversions of 20 to 30%, there is insufficient solvent to keep all of the polymer in solution. The importance of precipitation, if the data has been interpreted correctly, has already been discussed in connection with the solvent effect and could be equally important in the conversion effect.

Finally, it appears that pendent anhydride units may interchange with each other to give a monomeric unit and an intramolecular anhydride unit in the polymer chain:



This interchange has been noted by Hwa, Fleming, and Miller [6] and is probably due to the instability of unsymmetrical anhydrides. Their work shows that the bulk polymerization of acrylic propionic anhydride gives soluble poly(acrylic anhydride) and a liquid which was assumed to be propionic anhydride. In order to verify the nature of this liquid, a similar study was undertaken here in which methacrylic-propionic anhydride was prepared. By polymerization in bulk at 35°C and subsequent gas liquid chromatography on the liquid left, it was found that approximately 10% of the propionic anhydride units had undergone interchange during the polymerization. At 80°C, 20 to 30% of the anhydride units had interchanged. These results support the assumption of Hwa, Fleming, and Miller and add the possibility that methacrylic anhydride pendent units may undergo similar interchanges. Since the interchange is temperature dependent, it would be more important in polymerizations at high temperature.

To summarize, it appears that the increase in the observed value of cyclization with conversion is in fact due only in part to actual cyclization during polymerization. Decreasing monomer concentration and increasing heterogeneity actually cause increased cyclization, but cross-linking and pendent anhydride interchange increase the observed value of cyclization due to their ability to remove unsaturated units from the polymer chain.

Nonconjugated Chromophoric Interactions

Butler and Brooks [14], in a study of the UV spectra of nonconjugated dienes, observed that the absorption maximum for methacrylic anhydride is shifted bathochromically from those of ethyl, allyl, and methallyl methacrylate. It was suggested that the bathochromic shift was in the direction expected if interaction of nonconjugated double bonds in the excited state existed. If indeed this shift was due to double bond interaction, it would be evidence in support of a lower activation energy for the intramolecular propagation step in methacrylic anhydride. If this initial study and the suggested explanation are correct, there would be direct contradiction between the kinetic study (which indicates a higher activation energy for the cyclic step in methacrylic anhydride) and the UV study. In order to resolve the apparent discrepancy between these studies, a thorough UV spectral investigation of acrylate and methacrylate esters and anhydrides was undertaken.

A comparison of the values for the wavelength maxima and extinction coefficient obtained here (Table 7) with those given earlier [14]

TABLE 7. Ultraviolet Spectral Study[a]

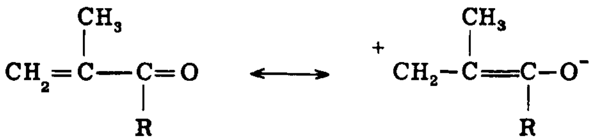
Compound	Wavelength maxima λ_{max} (nm)	Extinction coefficient
Methyl methacrylate	201.5	8600 (10350) [15]
Allyl methacrylate	201.5	10100
Vinyl methacrylate	205.7	12200
Methacrylic anhydride	209.0	19100
Methacrylic propionic anhydride	209.0	9700
Acrylic methacrylic anhydride	201.5	18300
Acrylic anhydride	199.5	20400
Methyl acrylate	191.0	10700
Ethyl acrylate [15]	192.3	14200

[a] Solvent, isooctane; cell, 0.01 cm far-UV silica; [M], 1×10^{-2} M to 1×10^{-3} M; instrument, Beckman DK-2A far-UV ratio recording spectrophotometer under nitrogen flush.

shows considerable differences. On reinvestigation it was found that the differences were due to instrumental limitations during the earlier work. The accuracy failure was quite pronounced below 210 nm and appears to have been due to excess stray light, quartz optics, and partial photomultiplier failure. Even though the earlier values are in error, both this work and the earlier work show that the bathochromic shift for methacrylic anhydride relative to its esters is real.

In an attempt to evaluate the earlier explanation [14] for the bathochromic shift, the unsymmetrical anhydride, methacrylic-propionic anhydride, was prepared and its structure proved. This anhydride is similar to methacrylic anhydride but has only one double bond; therefore, if the earlier explanation is correct, the unsymmetrical anhydride should have a wavelength maximum similar to the methacrylate esters. However, as is seen in Table 7, methacrylic and methacrylic-propionic anhydrides have the same absorption maxima and, as would be expected, the extinction coefficient for methacrylic anhydride is twice that of its unsymmetrical counterpart. These results indicate that the bathochromic shift is not due to excited state non-conjugated interaction between double bonds; therefore, there apparently is no contradiction between UV and kinetic data concerning the activation energy of the intramolecular propagation step relative to the intermolecular step. Further examination of the available data tends to indicate that the bathochromic shift is due to electronic stabilization through partial resonance of the nonbonded electrons on the anhydride oxygen with the carbonyl group. To add support to this suggestion, the UV spectrum of vinyl methacrylate was obtained. Since this compound has an unsaturated group attached to the ester oxygen, a stabilization similar to that observed for methacrylic anhydride should result in a bathochromic shift compared to methyl methacrylate. Table 7 shows that vinyl methacrylate is bathochromically shifted by 4 nm, about one-half the shift observed for the anhydrides. To gain a clearer overall picture of the reason for the bathochromic shift when an unsaturated group is attached to the acrylate and methacrylate ester or anhydride oxygens, it is useful to look at the reasonable resonance forms that may be involved in the electronic transition from ground to excited state.

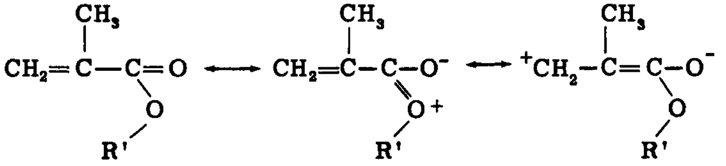
The two most important resonance forms involved in a $\pi\pi^*$ transition of an α,β-unsaturated system are



$$\underset{\text{I}}{CH_2{=}\overset{\overset{\displaystyle CH_3}{|}}{C}{-}\underset{\underset{\displaystyle R}{|}}{C}{=}O} \longleftrightarrow \underset{\text{II}}{\overset{+}{C}H_2{-}\overset{\overset{\displaystyle CH_3}{|}}{C}{=}\underset{\underset{\displaystyle R}{|}}{C}{-}O^-}$$

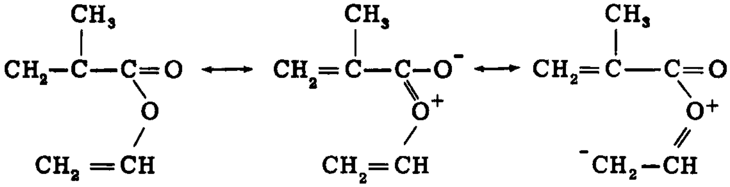
I II

In the ground state, Structure I is undoubtedly the most important resonance form with a small contribution from II. In the excited state, however, Form II becomes most important [16-18]. Although these two resonance forms are basic to the $\pi\pi^*$ transition, other resonance forms involving the R group can influence the relative energy of the ground and excited states which would shift the absorption maximum. Some of the resonance structures which may be important in altering the relative difference in energy from the ground to the excited states are

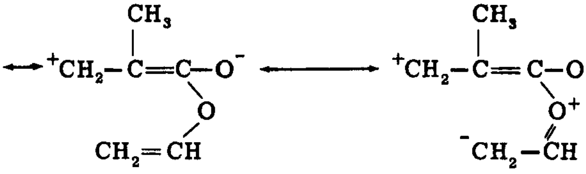


III IIIA IIIB

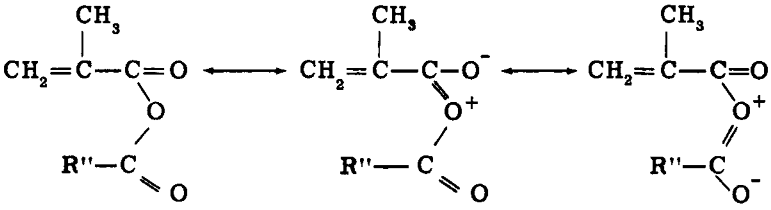
R' = alkyl or allyl



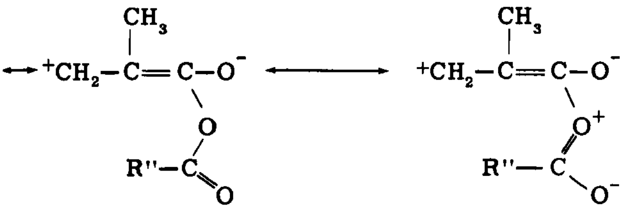
IV IVA IVB



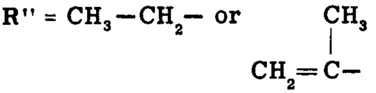
IVC IVD



V VA VB



VC VD



$R'' = CH_3{-}CH_2{-}$ or $CH_2{=}\overset{\displaystyle CH_3}{\overset{|}{C}}{-}$

As discussed above, III, IV, and V are probably the most representative ground state structures that can be drawn for saturated or allyl methacrylate esters, vinyl methacrylate, and methacrylic or methacrylic-propionic anhydrides. If III, IV, and V are the largest contributors to the ground state, then except for small inductive differences through the anhydride and ester oxygens, the electrons in the α,β-unsaturated systems must be of similar energy. In the excited state, however, it will be noted that there are only two resonance forms of similar energy for III whereas there are four for both IV and V. Evidently the added delocalization present when an unsaturated group is attached to the methacrylate acyl oxygen stabilizes the excited state of the molecule which is observed in the UV spectra as a bathochromic shift. This explains why vinyl methacrylate (IV) and methacrylic anhydride (V) show bathochromic shifts when compared to methyl or allyl methacrylate (III).

To explain the reason for the larger shift (8 nm) of methacrylic anhydride compared to vinyl methacrylate (4 nm), another examination of the resonance structures is necessary. While it is noted that both IV and V have four important excited state resonance forms and that Structures IVB and IVD are similar to VB and VD, it is immediately recognized that the relative contribution to the energy of their respective systems must be quite different. The reason for this difference is that a negative charge is developed on carbon in IVB and IVD while in VB and VD it develops on oxygen. Since oxygen is more electronegative than carbon, the negative charge is more stable and resonance forms VB and VD gain added importance. Apparently, it is this added stabilization and subsequent increased importance of VB and VD that results in the larger bathochromic shift for methacrylic anhydride.

Stereochemistry

Soon after proving the validity of the mechanism of cyclopolymerization, Crawshaw and Butler [19] noted that poly(acrylic acid) derived from the cyclopolymerization of acrylic anhydride had substantially higher degrees of crystallinity than that obtained from acrylic acid monomer. Recently, the discovery of stereochemical control in the cyclopolymerization of acrylic anhydride has received further support. Mercier and Smets [2] have shown in an IR study using model compounds, meso and racemic α,α'-dimethyl glutaric anhydrides, that acrylic anhydride polymerized in dimethylformamide at low temperature or cyclohexanone at high temperature is predominately isotactic; while, at low temperature in cyclohexanone, syndiotactic polymer was obtained. It was also noted that the syndiotactic polymer could be converted, presumably through α-hydrogen-carbonyl enolization, to the more stable isotactic form by heating the polymer in cyclohexanone. This tends to indicate that the kinetic or syndiotactic product is always formed but that it can be isomerized to the thermodynamic or isotactic product through either the catalytic influence of a solvent such as dimethylformamide or high-temperature polymerization in cyclohexanone.

In order to study the extent of the stereoregulating control, which had been exhibited in cyclopolymerization of acrylic anhydride, Miller, Brey, and Butler [20] studied the taciticy of poly(methyl methacrylate) derived from poly(methacrylic anhydride) as a function of polymerization temperature. The methacrylic anhydride system was chosen in this study due to: 1) the ease with which poly(methacrylic anhydride) can be converted to poly(methyl methacrylate), and 2) the availability of a quantitative method using NMR to ascertain the stereochemical configuration of the poly(methyl methacrylate). The results of the investigation by Miller, Brey, and Butler [20] indicate that the penultimate unit influences the placement of succeeding monomer units.

Butler [23] considered the types of propagating steps which are possible in cyclopolymerization in attempting to explain these results [20]. He suggested that a tendency of the cyclized radical to remain nonplanar at low temperatures, due to ring strain required by planarity, favors axial propagation which leads to predominant syndiotactic or heterotactic sequences. As the polymerization temperature rises, the energy necessary for a planar cyclized radical is available and results in increasing numbers of equatorial propagations leading to isotactic placements.

Tiers and Bovey [24] found very little difference in poly(methacrylic anhydride) prepared at 100°C using benzoyl peroxide and toluene solvent, and that obtained at -45°C using gamma irradiation and bulk conditions. Since so many variables (solvent, temperature, concentration, and initiator) are involved, the real significance of these results is questionable.

Since the literature dealing with the possible stereochemical significance of cyclopolymerization is rather limited and that which is available lacks consistency in results, a systematic study of the influence of temperature, solvent, monomer concentration, and conversion on the taciticity of poly(methacrylic anhydride) was undertaken to complete the study of methacrylic anhydride for this paper.

Using equal weights of methacrylic anhydride and cyclohexanone or dimethylformamide, polymer was obtained at various temperature, hydrolyzed, methylated, and subjected to NMR analysis. Table 8 shows the results of this analysis. Examination of these data indicates that within experimental error there is neither a temperature nor solvent effect on the tacticity. Further understanding of the data in Table 8 may be obtained through a study of the α values [22, 25]. If the system is "sigma," then the end unit of the methacrylic anhydride polymer chain will control the configuration of the next monomer unit added. The probability that the new unit will have the same configuration as the end unit is α. If the probability treatment is valid: $P_i = \alpha^2$, $P_s = (1 - \alpha)^2$, and $P_h = (\alpha - \alpha^2)$. Taking a representative value for α from Table 8 of 0.4, it is found that $P_i = 0.16$, $P_s = 0.36$, and $P_h = 0.48$ if the system is "sigma." As can be seen, these values correspond very

TABLE 8. Tacticity of Poly(methyl Methacrylate) Derived from Poly(methacrylic Anhydride) as Determined by NMR[a]

Solvent[b]	Polymerization temp (°C)	Conversion (%)	i(%)	h(%)	s(%)	α, Based on i peak
C	-40	40	15	32	53	0.39
C	0	45	15	42	43	0.39
C	20	43	11	38	51	0.33
C	80	46	13	41	46	0.36
D	20	45	19	37	44	0.43
D	40	48	16	38	46	0.40
D	60	35	20	40	40	0.45
D	90	51	16	39	45	0.40

[a] [Methacrylic anhydride], 50/50 by weight; [benzoin], 0.25 wt% based on methacrylic anhydride.

[b] Solvent: C = cyclohexanone; D = dimethylformamide.

closely to those obtained experimentally, indicating that the polymerizations of equal weights of methacrylic anhydride and cyclohexanone or dimethylformamide are "sigma" systems.

The meaning of the data on the stereochemical configuration of methacrylic anhydride as it relates to cyclopolymerization was clouded further when the kinetic study described previously indicated that at low conversion large numbers of noncyclic methacrylic anhydride units would be present when equal weights of monomer and solvent were polymerized. In order to eliminate the possibility of complicating results due to noncyclic units, a second study was undertaken using 0.2 mole/liter of methacrylic anhydride. This low monomer concentration insures that the fraction of cyclic units, even at low conversion, will be 0.9 or better. The results of this low concentration study in benzene, cyclohexanone, and dimethylformamide are given in Table 9. Analysis of the data indicates that there is no solvent effect on tacticity. The influence of conversion appears to be

TABLE 9. Tacticity of Poly(methyl Methacrylate) Derived from Poly(methacrylic Anhydride) as Determined by NMR[a]

Solvent[b]	Polymerization temp (°C)	Conversion (%)	i(%)	h(%)	s(%)	α, Based on i peak
B	10	54	21	44	35	0.46
B	50	32	17	42	41	0.41
B	50	42	18	46	36	0.43
B	50	88	19	48	33	0.44
B	80	63	19	45	36	0.44
C	10	99	19	42	39	0.44
C	50	98	21	42	37	0.46
C	80	72	19	47	34	0.44
D	10	77	18	42	40	0.43
D	50	73	19	42	39	0.44
D	80	35	19	48	33	0.44

[a] [Methacrylic anhydride], 0.2 mole/liter; [benzoin], 0.25 wt% based on methacrylic anhydride.

[b] Solvent: B = benzene; C = cyclohexanone; D = dimethylformamide.

small though, as is seen in the three benzene samples prepared at 50°C (Table 9), there is a small increase in heterotacticity with a corresponding decrease in syndiotactic character as the conversion is increased. There does not appear to be a temperature effect for samples polymerized in benzene, whereas in cyclohexanone there is a slight increase in heterotactic character and a parallel decrease in syndiotacticity with increasing temperature. Taking a representative value of α equal to 0.44, it is found that $P_i = 0.19$, $P_h = 0.31$, and $P_s = 0.50$ from the probability treatment. In comparing these values with those obtained experimentally, it is recognized that polymerization at low monomer concentration gives "nonsigma" results. This indicates that the end group is not the only factor contributing to the configuration of the unit being added, and corresponds in this respect to the results obtained by Miller, Brey, and Butler [20].

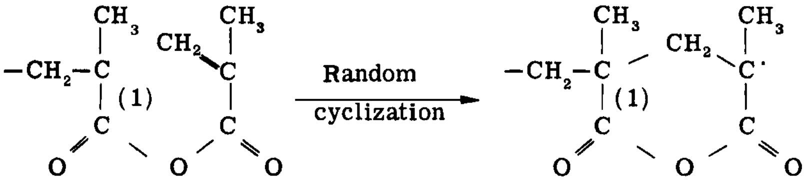
It is interesting to compare the tacticities of poly(methacrylic anhydride) obtained at high monomer concentrations (Table 8) and those at low concentrations (Table 9). This comparison shows that there is only a slight difference in isotactic sequences, but it is noted that the polymerizations at low concentration give 5 to 10% higher values for heterotactic character and 5 to 10% lower value for syndiotacticity than is obtained at high concentration. The explanation for these differences appears to be due to the incorporation of some noncyclic units in the poly(methacrylic anhydride) prepared at high monomer concentration. The noncyclic units would be expected to enter the polymer chain in stereochemical configurations similar to those observed in the free radical polymerization of methyl methacrylate (Table 10). Since poly(methyl methacrylate) gives large amounts of syndiotactic character, it might be concluded that noncyclic methacrylic anhydride units should increase the amount of syndiotacticity and decrease the heterotacticity. This is exactly what is observed when Tables 8 and 9 are compared.

In analyzing the data in Table 9, which presumably represents the stereochemical configuration of a completely cyclic polymer, two

TABLE 10. Structure of Polymers of Methyl Methacrylate Prepared with Free Radical Initiators [22]

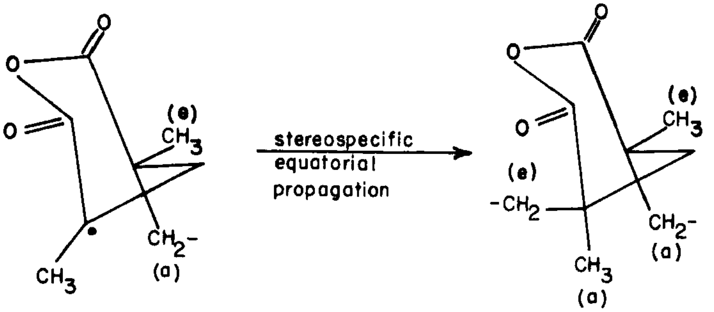
Polymerization conditions	i (%)	h (%)	s (%)
Irradiation in bulk, 0°C.	7.5	30.0	62.5
Benzoyl peroxide in bulk, 100°C.	8.9	37.5	53.9

factors are noticed. First, as has been discussed, the system is "nonsigma." Second, the heterotactic or duosyndiotactic character predominates over a slightly smaller percentage of syndiotactic character, which in turn is roughly twice as large as the isotacticity. These two factors, coupled with the fact that noncyclic units increase the syndiotactic character, tend to indicate that the cyclization step in cyclopolymerization is completely random with respect to the configuration:



Probability of e(d) = a(ℓ) at carbon (1)

In the intermolecular propagation step, however, there is stereospecific placement of the monomer unit. The stereospecific process is split in two parts. First, if the cyclization step resulted in an axial conformation then, due to steric restrictions which eliminate axial-axial propagations in one ring, the intermolecular propagation step will be equatorial.



Second, if the cyclization step results in an equatorial conformation, there will be competition between equatorial and axial propagation in the intermolecular step. If it is accepted that the cyclization step is completely random and the intermolecular propagation is stereospecifically equatorial when the cyclization step resulted in an axial conformation, it can be shown (Table 11) that a random intermolecular propagation, when cyclization resulted

TABLE 11. Probability Treatment of Tacticity in Poly(methacrylic Anhydride)[a]

Ring I[b] (1)	Ring I[b] (2)	Ring II (1)[c]	Ring II (2)[d]	Possible[e] configuration	Stereoregular form		Total i	Total h	Total s
a(ℓ)	(d)e	e(d)	(d)e	ℓddd	b	i	4	8	6
			(ℓ)a	ℓddℓ	h	h			
		a(ℓ)	(d)e	ℓdℓd	s	s			
							Probabilities		
							Pi	Ph	Ps
e(d)	(d)e	e (d)	(d)e	dℓdd	s	h			
			(ℓ)a	dℓdℓ	s	s			
		a(ℓ)	(d)e	dℓℓd	h	h	0.22	0.45	0.33
		(ed)	(d)e	dddd	i	i			
e(d)	(d)e		(ℓ)a	dddℓ	i	h			
		a(ℓ)	(d)e	ddℓd	h	s			

[a] Conformations: a = axial; e = equatorial. Configurations: d = dextrorotatory; ℓ = laevoratatory. Tacticities: i = isotactic; s = syndiotactic; h = heterotactic.

[b] Ring I: All possible starting ring conformations.

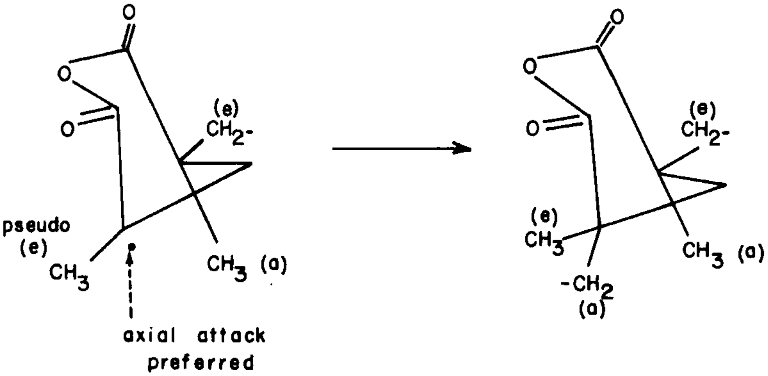
[c] Ring II-(ℓ): Random a(ℓ) or e(d) cyclization.

[d] Ring II-(a): Intermolecular step random e(d) or a(ℓ) if Ring II-(1) is e(d); but stereospecific e(d) if Ring II-(1) is a(ℓ).

[e] ℓℓℓ or ddd, isotactic; ℓdℓ or dℓd, syndiotactic, ℓℓd or ddℓ, heterotactic or duosyndiotactic.

in an equatorial conformation, will lead to the following probabilities for each type sequence: $P_i = 0.22$, $P_h = 0.45$, and $P_s = 0.33$.

A comparison of the probabilities obtained in this theoretical treatment (Table 11) with those observed experimentally (Table 9) shows that the theoretical value for the isotactic probability is slightly high while that for the syndiotactic sequence is low by a similar amount. This tends to support Butler's [23] suggestion that considerable ring strain would result if the cyclized radical was planar; therefore, axial propagation is favored since the α-methyl at the radical-carbon tends to occupy an equatorial position. Since the axial propagation is favored, there will be a slight increase in the amount of syndiotactic and heterotactic character with a corresponding decrease in isotactic sequences.



The explanation of the experimental results shows that Hwa's [26] conclusion that the cyclic propagation step is random and the intermolecular step always results in trans (ae or ea) propagation is partially correct. However, the evidence gathered shows that, although the trans (ae or ea) propagation is highly favored, there are significant numbers of cis (ee), but no (aa), propagations. Further, probably due to the stereospecific intermolecular propagation, when the cyclic step results in an axial chain conformation, the methacrylic anhydride system exhibits "nonsigma" behavior.

To summarize, it appears that cyclopolymerization of methacrylic anhydride does result in at least one stereospecific propagation step which explains the reason for the "nonsigma" relationship and the high degrees of heterotactic and syndiotactic character. Actually, since the high degree of heterotacticity results from a partially stereospecific process, it is probably better to term this sequence duosyndiotactic to avoid the connotation that it developed through a random process. The importance of recognizing that cyclopolymerization gives a unique and different stereochemical configuration has been emphasized by the discovery [27] that poly(methyl methacrylate) derived of poly(methacrylic anhydride) has a higher monolayer collapse pressure (33 dynes/cm) than poly(methyl methacrylate) prepared by conventional polymerization processes. This high collapse pressure indicates that cyclopolymerization results in the tightest packing and toughest film possible. Butler's [23] explanation for the observed tacticities in the work of Miller, Brey, and Butler [20] seems to be applicable to both the results obtained here and those reported by Hwa [27]; the results of both this work and Hwa's work substantiate Butler's suggestion that the stereochemical configuration obtained in cyclopolymerization is a result of a minimization of ring strain and steric interaction of neighboring rings.

The results of the stereochemical study also show that there is little or no solvent effect on the stereoregular configuration, but that there is apparently a small increase in heterotacticity and a corresponding decrease in syndiotacticity with increasing conversion and temperature. Further, it was found that polymerization at high monomer concentration results in an increase in syndiotactic character at the expense of isotactic and heterotactic sequences. This appears to result from incorporation of noncyclic anhydride units along the polymer chain which, like methyl methacrylate, give predominantly syndiotactic sequences.

EXPERIMENTAL

Equipment and Data

The temperatures reported are uncorrected and in degrees centigrade. Pressures are expressed in millimeters of mercury as determined by means of either a Zimmerli or McLeod gauge. Refractive indices were determined with a Bausch and Lomb Abbe 34 Refractometer equipped with an achromatic compensating prism. Intrinsic viscosities were calculated from efflux times of benzene solutions of poly(methyl methacrylate) through a Connon-Ubbelohde Semi-micro Dilution Viscometer set at 25°C in a constant temperature bath. Gas-liquid chromatography (GLC) analyses were made with a Wilkens Aerograph Model A-110-C Gas Chromatographic Instrument using helium for eluent gas and a 5-ft column packed with 20% Silicon GE SF-96 on firebrick. Infrared spectra were obtained with a Perkin-Elmer Infracord Double-beam Infrared Recording Spectrophotometer or a Perkin-Elmer Model 21 Double-beam Infrared Recording Spectrophotometer. Both were equipped with sodium chloride optics and calibrated with polystyrene film. All UV spectra were obtained with a nitrogen flushed Beckman Model DK-2A Ratio Recording Spectrophotometer equipped with far-UV silica optics and cells. Wavelengths were calibrated with the emission lines of mercury. Nuclear magnetic resonance (NMR) spectra were obtained with a Varian V-4302 High Resolution Nuclear Magnetic Resonance Spectrometer, operating at 56.4 Mc. Sample temperature was maintained at 90-100°C during the measurements. X-ray diffraction spectra were obtained with a Norelco X-ray Diffractometer Model 12045 using a proportional counter. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tennessee.

Kinetic Study

Polymer Preparation.

Methacrylic anhydride of the desired concentration in benzene, cyclohexanone, or dimethylformamide was prepared in volumetric flasks of the appropriate size. These solutions were added, by means of a funnel, to cleaned and dried Kimble Neutraglas 20 or 50 ml ampules containing 0.25 wt% of benzoin based on the methacrylic anhydride concentration. While under dry nitrogen gas flush, the sample ampule was cooled in a Dry-Ice and acetone bath and sealed with a natural gas-oxygen torch. After sealing, the ampules were placed just beneath the surface of a constant temperature bath (+100 to -60 ± 0.1°C). When at constant temperature the samples were irradiated with a Blak-Ray XX-15 long wavelength UV lamp from a distance of 4 to 8 in. The time necessary to obtain a desired conversion was determined by trial-and-error. The sample was isolated by breaking open the ampule and pouring its contents into rapidly stirred diisopropyl ether. Approximately 10 parts ether to 1 part sample were used. It must be emphasized that the ether must be exceedingly dry and not contain any traces of base (such as from drying with sodium) if results are to be accurate and reproducible. The ether-precipitated polymer is filtered off with a sintered glass filter and dried 24 hr in vacuo at 50 to 60°C.

The amount of poly(methacrylic anhydride) necessary to give 0.002 equivalents of unsaturation was weighed accurately and hydrolyzed. Hydrolysis was obtained by refluxing two pellets of reagent-grade sodium hydroxide in 100 ml of distilled water for each 0.5 g of sample present. When hydrolysis was complete, as evidenced by the sample dissolving, the solution was cooled, 1 drop of phenolphthalein added, and neutralized by dropwise addition of 6 $\underline{N}$ sulfuric acid.

Bromometric Titration

The method described by Siggia [28] for bromination of unsaturated compounds was used to determine the fraction of cyclic units in poly(methacrylic anhydride) samples.

For comparison with the sample, a blank was run using the same procedure except that a neutralized hydrolysis solution without polymer was used as the sample.

The equation used for the calculation of the fraction of cyclic units (f_c) was:

$$f_c = 1 - \frac{(V_b - V_s)(N)(MW)}{(wt)(2000)(B)}$$

where V_b = milliliters of thiosulfate for blank.
V_s = milliliters of thiosulfate for sample.
N = normality of sodium thiosulfate.
MW = molecular weight of sample.
wt = weight of sample used.
B = number of moles of bromine being absorbed.

The reproducibility of the above procedure was checked for the poly(methacrylic anhydride) system. It was found that various concentrations of standard methacrylic acid-poly(methacrylic acid) solutions could be determined accurately (±1 to 20%) if 0.002 equivalents of unsaturation were present. The accuracy appeared to be as good as ±2 to 4% down to 0.001 equivalents.

The results of the low conversion study of the fraction of cyclic units as a function of concentration, temperature, and solvent have been listed earlier (Tables 1, 2, and 5, respectively). The results of the study at high conversions are shown in Table 12.

TABLE 12. High Conversion Study of the Fraction of Cyclic Units as a Function of Temperature and Solvent[a]

Solvent[b]	Polymerization temp (C)	Conversion (%)	f_c
B	0	37	0.88
B	80	73	0.94
C	-60	45	0.85
C	40	49	0.90
C	100	57	0.87
D	10	33	0.92
D	30	43	0.95
D	50	47	0.87
D	80	35	0.89
D	100	43	0.95

[a] [Methacrylic anhydride], 50/50 by weight; [benzoin], 0.25 wt% based on methacrylic anhydride.

[b] Solvent: B = Benzene; C = Cyclohexanone; D = Dimethylformamide.

In order to avoid errors in accuracy, several variables were checked. First, by using standard solutions of methacrylic acid-poly(methacrylic acid), the hydrolysis procedure was checked and found not to influence the results. Second, several samples of poly(methacrylic anhydride) were dissolved, reisolated, and dried to check for trapped monomer. The results showed that the first isolation was sufficient to remove all monomer.

Preparation of Methacrylic-Propionic Anhydride

The procedure described by Yakubovich [29] was used for the preparation of this mixed anhydride. Distillation gave 72 g of a pure colorless liquid, bp 28-29°C/0.5 mm, n_D^{20} 1.4300, d_4^{20} 1.023.

The structure of the product was proved by IR and elemental analyses. The IR spectra of the distillate showed the following absorption bands: 1806 and 1731 cm^{-1} (C=O); 1638 cm^{-1} (C=C). For comparison a solution (1:1 mole ratio) of methacrylic and propionic anhydrides was prepared. The mixture showed four absorption bands in the carbonyl region: two for methacrylic anhydride, 1787 and 1730 cm^{-1} (C=O); two for propionic anhydride, 1818 and 1752 cm^{-1} (C=O). The comparison of the liquid obtained in the reaction to the known mixture showed that the mixed anhydride had been made and was not a mixture of the two symmetrical anhydrides. Elemental analysis also corresponded to the proposed structure.

Analysis: Calculated for $C_7H_{10}O_3$: C, 59.14; H, 7.09. Found: C, 58.95; H, 7.04.

Polymerization of Methacrylic-Propionic Anhydride

A 20-ml Kimble Neutraglas ampule was charged with 5.10 g of methacrylic-propionic anhydride and 0.0154 g of benzoin, flushed with dry nitrogen gas, cooled in Dry-Ice and acetone, and sealed. The sealed ampule was placed in a constant temperature bath set at 30°C and irradiated with a Blak-Ray XX-15 long wavelength UV lamp for 30 min. The sample was broken open and liquid decanted into a screw-top vial. The weight of the liquid indicated a conversion of 60%. Similar irradiation of a second ampule for 20 min at 80°C gave 65% conversion.

The liquid decantate was analyzed by IR spectra and GLC. Both samples showed the presence of extra carbonyl peaks in the carbonyl region, showing that some symmetrical propionic anhydride was present.

GLC on the pure methacrylic-propionic anhydride shows that it isomerizes in the injector block to give the two peaks corresponding to the symmetrical anhydrides. However, by taking the increase in size of the peak corresponding to propionic anhydride relative to that for methacrylic anhydride, it was found that at 30°C approximately

10% of the propionic pendent groups had interchanged to give symmetrical propionic anhydride and presumably an intramolecular anhydride unit in the polymer. At 80°C, approximately 20 to 30% had undergone the interchange reaction (see the earlier discussion of the significance of the interchange).

Preparation of Acrylic-Methacrylic Anhydride

This compound was prepared by the procedure described by Hwa [6]. Distillation gave 26.5 g of a colorless liquid, bp 33 C/0.7 mm, n_D^{20} 1.4517 (1.4516 Hwa [6]), and d_4^{20} 1.056. Infrared showed absorption bands at 1790 and 1730 cm^{-1} (C=C); 1633 cm^{-1} (C=C). Since the carbonyl absorption bands for methacrylic (1787 and 1730 cm^{-1}) and acrylic (1797 and 1734 cm^{-1}) anhydrides were not sufficiently separated to give four carbonyl peaks when a 1:1 mole mixture of the anhydrides was made, the structure proof for acrylic-methacrylic anhydride could not be made complete. However, its structure was partially substantiated by GLC which showed equal amounts of acrylic and methacrylic anhydrides present, and the properties were the same as those described by Hwa [6].

Ultraviolet Spectral Investigation

All compounds studied (see Table 7) were fractionally distilled until their properties coincided with values in the literature, where available, and, in addition, showed a purity of 99+% by GLC and IR spectra (Table 13). The absorption curve for each compound was taken at three or more concentrations in the range 1×10^{-2} to 1×10^{-3} $\underline{M}$. In each case Beer's law was obeyed within the concentration range used. The absorptivity value, a, was calculated from the equation $A = abc$, where A is the absorption of the sample corrected for the solvent blank; a is the absorptivity, b is the cell thickness, which was 0.01 cm in each case; and c is the concentration given in mole/liter of compound.

Preparation of Diazomethane

Use no ground-glass joints! All connections are rubber and set-up was made in an efficient hood. In a 1-liter, round-bottom, distilling flask was placed a large magnetic stirrer, 200 ml of reagent-grade benzene, and 240 ml of 40% aqueous sodium hydroxide. The side-arm of the flask was connected to a condenser, which was connected to a 1-liter Erlenmeyer flask in series with a 250-ml Erlenmeyer flask. Both receiver flasks were cooled to 5°C, and this temperature was maintained. The neck of the distilling flask was equipped with a 500-ml separatory funnel containing 28.4 g of DuPont EXR-101 in 500 ml of benzene. An oil bath was raised under the distilling flask, stirring started, and slow distillation of benzene attained. As soon as the

TABLE 13. Physical Properties

				Infrared absorption[a] (cm^{-1})	
Compound	bp (C/mm)	n_D^{20}	d_4^{20}	C=O	C=C
Methyl acrylate	80.5/760	1.4033	0.954	1732	1635, 1622
Methyl methacrylate	43.5/87	1.4150	0.944	1728	1642
Allyl methacrylate	43.5/14	1.4372	0.9339	1728	1642
Vinyl methacrylate	49/60	1.4029	-	1739	1646
Methacrylic anhydride	48/1	1.4541	1.0315	1787, 1730	1639
Methacrylic-propionic anhydride	28-29/0.5	1.4300	1.023	1806, 1731	1638
Acrylic-methacrylic anhydride	33/0.7	1.4517	1.056	1790, 1730	1633
Acrylic anhydride	68/10	1.4484	1.0811	1797, 1734	1631
Propionic anhydride	167.5/760	1.4040	1.011	1818, 1752	-

[a] The IR spectra were obtained on the pure liquid using a Perkin-Elmer Model 21 Double-beam Infrared Recording Spectrophotometer.

benzene was distilling steadily, the mixture in the separatory funnel was stirred and 10 to 15 ml added to the reaction mixture. Immediate evolution of diazomethane resulted as evidenced by the yellow color of the benzene distillate. As soon as the yellow color disappeared, the mixture in the funnel was stirred again and another 10 to 15 ml added. This procedure was continued until all of the EXR-101 was added and the distillate had become colorless again. Distillation was stopped and the solutions of diazomethane in the two receivers combined. The diazomethane was decanted off the water, which had azeotroped, and carefully divided among the samples of poly(methacrylic acid). The yield was generally about 80% of theory or about 5.4 g (0.13 mole).

Stereochemistry Study

Polymer Preparation

Methacrylic anhydride of the desired concentration (50/50 wt or 0.2 mole/liter) in benzene, cyclohexanone, or dimethylformamide was prepared in volumetric flasks of the appropriate size. By means of a funnel 0.25 wt% of benzoin and the methacrylic anhydride solutions were added to cleaned and dried Kimble Neutraglas 20 or 50 ml ampules. The ampules, while flushing with dry nitrogen gas, were cooled in a Dry-Ice and acetone bath and sealed with a torch. When sealed, the samples were placed just beneath the surface of a constant temperature bath set at the desired temperature and irradiated from a distance of 4 to 8 in. until the desired conversion was obtained (see Tables 8 and 9 for the results of these polymerizations). Since conversion was generally greater than 30%, the polymer was usually a gel or solid due to insufficient solvent to keep it in solution. In order to isolate the polymer, the ampule was broken and the gel or solid thoroughly ground with a mortar and pestle under dry diethyl ether. After grinding, the polymer was allowed to stand in ether for 4 to 6 hr and was then filtered off, washed with several 50 ml portions of ether, and dried in vacuo at 50 to 60 °C for 24 to 48 hr.

Hydrolysis of Poly(methacrylic Anhydride)

Since it had been found [20] that base hydrolysis does not cause racemization in the polymer, a mild solution of sodium hydroxide was used. A 0.5-g sample of poly(methacrylic anhydride) was hydrolyzed by placing it in 75 ml of distilled water containing two pellets of reagent-grade sodium hydroxide and refluxing 6 to 12 hr. The hydrolyzed polymer was poured into a beaker and heated on a steam bath while concentrated hydrochloric acid was added to precipitate the polymer. The poly(methacrylic acid) was filtered off using a sintered glass filter and dried in vacuo at 50 to 60° C. Conversion from anhydride to acid, including recovery, was generally in the range of 90 to 100%.

Esterification of Poly(methacrylic Acid)

The method used for esterification was essentially the same as that described by Katchalsky [30] using 0.3 g (0.0035 mole) samples of poly(methacrylic acid). The product was dried in vacuo at 50 to 60° C for 24 to 48 hr. Although esterification was undoubtedly complete, isolation of all poly(methyl methacrylate) was very difficult and generally only 80% recovery was obtained.

Preparation of Samples for Nuclear Magnetic Resonance Analysis

Glass tubing (18 × 0.5 cm) was sealed at one end and dried in a 130° C oven. Samples of poly(methyl methacrylate) (0.07 to 0.08 g) were packed in the open end of the tubes and tapped to the bottom. With the aid of a hypodermic syringe, sufficient ethanol-free chloroform was added to give a 14% (w/v) poly(methyl methacrylate) solution. The filled tube was placed in a liquid nitrogen trap and vacuum applied. While under vacuum the sample was sealed. In order to assure that the tube was completely sealed, it was heated for 10 min in boiling water. The results of the NMR analysis run at 90 to 100° C on a Varian V-4302 High Resolution Nuclear Magnetic Resonance Spectrometer, operating at 56.4 Mc, are listed in Tables 8 and 9.

Attempts were made to run poly(methacrylic anhydride) in dimethylformamide and dimethylsulfoxide, but they were unsuccessful due to insufficient solubility of the anhydride and interference of the solvent hydrogens in the NMR spectra.

An attempt was also made to run poly(methacrylic acid) in distilled water. However, due to insufficient solubility, the intensity of the peaks was very weak and therefore useless in obtaining area traces of the stereochemical configurations.

X-ray Diffraction Study on Poly(methyl Methacrylate) Derived from Poly(methacrylic Anhydride)

The samples prepared at various polymerization temperatures were ground to a fine powder for the x-ray diffraction analysis. The results are listed in Table 14 and, as is seen, there is no measurable change in the degree of crystallinity with increasing temperature.

Molecular weights of Poly(methyl Methacrylate Derived from Poly(methacrylic Anhydride

Solutions of poly(methyl methacrylate) in benzene (1 g/100 ml) were prepared. Two milliliters of solution were placed in a Cannon-Ubbelohde Semi-micro Dilution Viscometer which was mounted in a

TABLE 14. X-Ray Diffraction Study of the Degree of Crystallinity as a Function of Polymerization Temperature on Poly(methyl methacrylate) Derived from Poly(methacrylic Anhydride)

Polymerization[a] temp (°C)	Conversion (%)	Peak position[b] 2θ (degrees)	Peak width at 1/2 peak height (degrees)
20	45	13.9 ± 0.2	8 ± 0.2
40	48	13.7 ± 0.2	7.9 ± 0.2
60	35	13.8 ± 0.2	8 ± 0.2
90	51	13.8 ± 0.2	7.7 ± 0.2

[a] Solvent, dimethylformamide; [benzoin], 0.25 wt% based on methacrylic anhydride; [methacrylic anhydride]; 50/50 by weight.

[b] X-ray wavelength: 1.544 Å.

constant temperature bath set at 25 ± 0.1°C. The efflux times of the original solution and at least three dilutions were taken. From these efflux times the intrinsic viscosity was found. By use of Baxendale's [31] equation, the conversion of intrinsic viscosity into molecular weight was made:

$$[\eta]_{25^\circ} = 0.75 \times 10^{-4}\ M^{-0.76}$$

for poly(methyl methacrylate) in benzene.

No trend of molecular weight with temperature could be found. Molecular weight did vary with solvent. For benzene and dimethylformamide the molecular weight was between 200,000 and 350,000. For cyclohexanone the molecular weight was much lower due to chain transfer, generally being between 50,000 and 100,000.

ACKNOWLEDGMENTS

The authors are indebted to Dr. W. S. Brey and his associates for the nuclear magnetic spectra reported in this study. One of us (T.F.G., Jr.) acknowledges with thanks the honor of being the recipient of a Chemstrand Fellowship and a Tennessee Eastman Fellowship during the course of this work.

REFERENCES

[1] G. B. Butler and K. B. Baucom, J. Macromol. Sci.—Chem., A8(7), 000 (1974).
[2] J. Mercier and G. Smets, J. Polym. Sci., A1, 1491 (1963).
[3] W. E. Gibbs and J. T. Murray, Ibid., 58, 1211 (1962).
[4] G. Smets, N. Deval, and P. Hous, Ibid., A2, 4835 (1964).
[5] M. S. Matheson, E. E. Auer, E. B. Bevilacqua, and E. J. Hart, J. Amer. Chem. Soc., 71, 497 (1949).
[6] J. C. H. Hwa, W. A. Fleming, and L. Miller, J. Polym. Sci., A2, 2385 (1964).
[7] J. C. Bevington and B. W. Malpass, Ibid., A2, 1893 (1964).
[8] G. Smets, P. Hous, and N. Deval, Ibid., A2, 4825 (1964).
[9] K. A. Stacey, Light-Scattering in Physical Chemistry, Butterworths, London, 1956, Chap. 4.
[10] J. C. Bevington, Radical Polymerization, Academic, New York, 1961, pp. 99-100.
[11] J. Mercier and G. Smets, J. Polym. Sci., 57, 763 (1962).
[12] P. Hayden and H. Melville, Ibid., 43, 215 (1960).
[13] J. C. H. Hwa and L. Miller, Ibid., 55, 197 (1961). J. Roovers and G. Smets, Makromol. Chem., 60, 89 (1963).

[14] G. B. Butler and T. W. Brooks, J. Org. Chem., 28, 2699 (1963).
[15] W. D. Closson, S. F. Brady, E. M. Kosower, and P. C. Huang, Ibid., 28, 1161 (1963).
[16] A. T. Nielsen, Ibid., 22, 1539 (1957).
[17] G. W. Wheland, Resonance in Organic Chemistry, Wiley, New York, 1955, Chaps. 3 and 6.
[18] H. H. Jaffe and Milton Orchin, Theory and Applications of Ultraviolet Spectroscopy, Wiley, New York, 1962, Chap. 10.
[19] A. Crawshaw and G. B. Butler, J. Amer. Chem. Soc., 80, 5464 (1958).
[20] W. L. Miller, W. S. Brey, Jr., and G. B. Butler, J. Polym. Sci., 54, 329 (1961).
[21] F. A. Bovey, G. V. D. Tiers, and G. Filipovich, Ibid., 38, 73 (1959).
[22] F. A. Bovey and G. V. D. Tiers, Ibid., 44, 173 (1960).
[23] G. B. Butler, Pure Appl. Chem., 4, 299 (1962).
[24] G. Tiers and F. Bovey, J. Polym. Sci., 47, 479 (1958).
[25] D. D. Coleman, Ibid., 31, 155 (1958).
[26] J. C. H. Hwa, Ibid., 60, S12 (1962).
[27] J. C. H. Hwa and H. E. Ries, Jr., Ibid., B2, 389 (1964).
[28] S. Siggia, Quantitative Organic Analysis via Functional Groups, Wiley, New York, 1949, pp. 33-37.
[29] A. Ya. Yakubovich, L. I. Muler, and M. V. Bazilevskii, Zh. Ohshch. Khim., 30, 1274 (1960).
[30] A. Katchalsky and H. Eisenberg, J. Polym. Sci., 6, 145 (1951).
[31] J. H. Baxendale, S. Bywater, and M. G. Evans, Trans. Faraday Soc., 42, 675 (1946).

Accepted by editor July 8, 1974
Received for publication July 31, 1974