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Head-to-Head Polymers. XXIII. Toward Head-to-Head Poly(methyl Methacrylate). Cyclopolymerization of Methacrylic Acid Derivatives: Hydrolysis and Esterification

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Head-to-Head Polymers. XXIII.* Toward Head-to-Head Poly(methyl Methacrylate). Cyclopolymerization of Methacrylic Acid Derivatives: Hydrolysis and Esterification

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ABSTRACT

N-Phenyldimethacrylamide was polymerized to a cyclopolymer which not only contains 94% five-membered rings, but more importantly also contains 6% six-membered rings in the cyclopolymer. In spite of extensive effort using drastic techniques of hydrolysis, the cyclopolymer could not be hydrolyzed to the polymeric acid. For comparison, dimethacrylic anhydride was cyclopolymerized under various conditions to produce polymers of various molecular weights which consisted essentially of six-membered rings in the polymer structure. It could be hydrolyzed and esterified to the polymeric methyl ester which was characterized by spectroscopic methods, particularly ^{13}C-NMR spectroscopy, and compared with conventional poly(methyl methacrylate).

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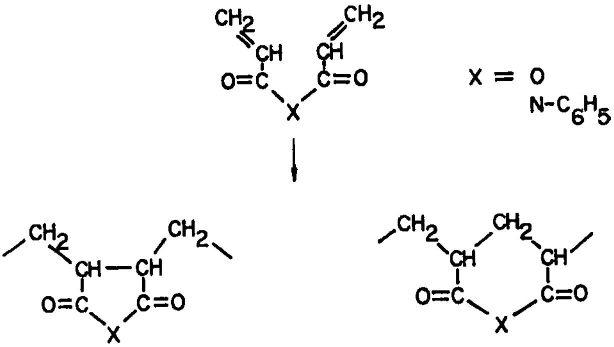
INTRODUCTION

One of the conceptual routes for the synthesis of pure head-to-head (H-H) poly(methyl methacrylate) (PMMA) requires that the well-known cyclopolymerization of methacrylic acid derivatives, such as methacrylic acid anhydride or N-dimethacrylamide derivates, leads entirely to high molecular weight cyclopolymers of units of five-membered rings (succinic acid derivatives) that can be quantitatively transformed to the dimethyl esters.

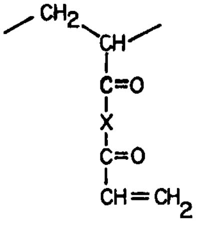
Other possible indirect routes for the preparation of pure H-H PMMA include the alternating copolymerization of 2,3-dimethylmaleic anhydride (DMMA) and ethylene [1] based on the work on the alternating copolymers of PMMA and methyl vinyl ethers [2, 3]. We attempted this approach but did not obtain alternating copolymers; the copolymers that were obtained were also of low molecular weight.

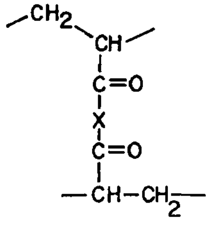
The preparation and description of properties of polymers with considerable H-H PMMA linkages have been described recently [4, 5].

Since the first discovery of cyclopolymerization, it was known that cyclopolymerization produced polymer structures with five-membered rings, six-membered rings, and noncyclized units, leaving a side chain with an olefinic double bond or cross-linked polymers if the second double bond also polymerized (Eq. 1). The formation of the type of such individual structural units depends very much on the type of α,ω-diene monomer that is used for the cyclopolymerization and, to some extent, on the reaction conditions under which the polymerization reaction is carried out [6-13]. Mechanistic considerations established that the stereochemistry of the individual monomeric units, thermodynamic and kinetic control during the polymerization, and the type of monomer structure determine the actual ratio of five-membered rings in the polymer structure:



(1)





Methacrylic acid derivatives are necessary in principle for the preparation of five-membered cyclopolymers that can be hydrolyzed and esterified to H-H PMMA. Five-membered ring cyclopolymers have been obtained in relatively high content by the cyclopolymerization of acrylic anhydride at 115°C in xylene [14]. Also, differences were observed in the carbonyl region in the infrared spectra between cyclopolymers from dimethacrylamides and polymers produced from polymethacrylamides [15]. It was concluded that the cyclopolymerization of dimethacrylamides gave predominantly five-membered ring units in the polymer. Accurate ^{1}H- or ^{13}C-NMR spectroscopy has not been carried out, and earlier work has consequently not been applicable for our specific problem of analyzing the details of the structure of cyclopolymers of methacrylic acid derivatives.

For the preparation of pure H-H PMMA it is required to have methacrylic acid derivative capable of cyclopolymerization which give only five-membered rings in the cyclopolymer structure and that do not have detectable amounts of six-membered rings or uncyclized units in the polymer chain. Both six-membered and noncyclized material, after hydrogen and esterification, lead to head to tail (H-T) linkages in the final polymers, which are undesirable for our purposes, even in the smallest amounts.

It was consequently the objective of this work to reevaluate cyclopolymerization of selected methacrylic acid derivatives, to analyze the purity of the cyclic structure, and to carry out hydrolysis and esterification experiments in attempts to synthesize H-H PMMA.

EXPERIMENTAL

Material

Aniline (Aldrich Chemical Co.), methacryl chloride (Aldrich Chemical Co.), methyl methacrylate (Aldrich Chemical Co.), and methacrylic acid (Aldrich Chemical Co.) were distilled under reduced pressure and nitrogen before use.

Tetrahydrofuran (Aldrich Chemical Co.) was heated to reflux over $LiAlH_4$ overnight and then distilled under nitrogen.

Benzene (MCB Manufacturing Chemists, Inc.) (reagent grade) was heated to reflux over sodium and distilled under nitrogen.

Sodium hydride (Ventron, Alfa Division) and acetic anhydride (Aldrich Chemical Co.) were used from freshly opened bottles. Diazald (Aldrich Chemical Co.) (N-methyl-N-nitroso-p-toluenesulfonamide, used to generate diazomethane) was used as received.

Azobisisobutyronitrile (AIBN) (Aldrich Chemical Co.) was purified by recrystallization three times from dry methanol and dried overnight at room temperature and 0.1 mm.

Benzoyl peroxide (BPO) (Aldrich Chemical Co.) was recryatallized three times from dry ethanol and dried overnight at room temperature at 0.1 mm.

Measurements

Infrared spectra were recorded on a Perkin-Elmer Model 727 spectrophotometer. The infrared spectra of poly(methacrylic anhydride) samples were measured as KBr pellets; the polymeric methyl esters were measured as films cast from chloroform solution onto a single sodium chloride plate.

The ^{1}H-NMR spectra were recorded on a 60 MHz-24 Hitachi Perkin-Elmer spectrometer. Poly(methacrylic anhydride) samples were measured in solutions of DMSO-d_6; the methyl esters were measured in $CDCl_3$ in concentrations of 10 to 15%. Poly(N-phenyldimethacrylamide) was measured on a Bruker WM 250 superconducting NMR spectrometer in $CDCl_3$.

^{13}C-NMR spectra were obtained on a Varian CFT-20 spectrometer under complete proton decoupling. The measurements were carried out in $CDCl_3$ or in DMSO-d_6 at room temperature with TMS as the internal standard.

A Perkin-Elmer DSC-2 Differential Scanning Calorimeter was used for the determination of the glass transition temperature (T_g) at a programmed temperature increase of 20°/min.

The molecular weight was measured by GPC using a Waters Model 201 chromatograph and calculated using polystyrene as the standard samples.

Elemental analyses were performed by the Microanalytical Laboratory, Office of Research Services, University of Massachusetts, Amherst, Massachusetts.

Preparations

N-Phenyldimethacrylamide (PhDMA). N-Phenyldimethacrylamide was prepared according to Butler's method [7, 8]. To a solution of 93 g (1.0 mol) of freshly distilled aniline in benzene (350 mL), a solution of freshly distilled methacryl chloride (52 g, 0.5 mol) in 50 mL of benzene was added dropwise over a period of 1.5 h under dry nitrogen and the mixture was stirred overnight. After the reaction was complete, water (500 mL) and benzene (160 mL) were added. The two layers were allowed to separate and the benzene layer was extracted with two parts of 1 N hydrochloric acid (100 mL), two 100-mL portions of 10% sodium carbonate, and dried over anhydrous sodium sulfate. Benzene was evaporated from the solution, the residue was recrystallized twice from n-hexane-acetone (2:1), and the solid after filtration was dried for 2 d at room temperature and 0.1 mm; yield 57 g (71%); mp 84-85°C.

To a 60% dispersion of sodium hydride (6.4 g) in mineral oil and THF (50 mL), a solution of 24.2 g (0.15 mol) of methacrylanilide in 50 mL of THF was added dropwise over a period of 3 h with stirring under nitrogen; stirring was continued for an additional hour. The solution of the sodium salt of methacrylanilide was added dropwise to a solution of 18.6 g of methacryl chloride and 75 mL of THF over a 4.5-h period; stirring was continued for an additional hour and then methanol (15 mL) was added. The reaction mixture was poured into n-hexane (500 mL), the solid filtered, and the solvent evaporated. The residue was recrystallized three times from anhydrous ether and dried at room temperature and 0.1 mm for 1 d. N-Phenyldimethacrylamide was obtained in a yield of 20.5 g (60%), mp 79.5-80.0°C.

Elemental analysis: Calculated for $C_{14}H_{15}NO_2$; C, 73.34%; H, 6.59%; N, 6.11%. Found: C, 73.39%; H, 6.71%; N, 6.14%.

Polymerization of N-phenyldimethacrylamide. The polymerizations of N-phenyldimethacrylamide were carried out with AIBN as the initiator in benzene solution or in the melt as follows: N-phenyldimethacrylamide (4 g) and 40 mg AIBN (1.0 wt% based on monomer) were dissolved in 8 mL of benzene. This solution was transferred to a 25-mL Pyrex polymerization tube; the tube was degassed by three freeze-thaw cycles (liquid nitrogen) before sealing it at 0.1 mm and placing it in a constant temperature bath at 50°C. After 4 d the tube was opened and the contents were poured into 200 mL of methanol. Poly(N-phenyldimethacrylamide) precipitated, was collected by filtration, washed three times with methanol, and dried overnight at 65°C and 0.1 mm; yield 2.0 g (50%); the inherent viscosity was 0.14 dL/g. The infrared spectrum showed the characteristic peaks of the cycloimide at 1710 and 1778 cm^{-1}. The glass transition temperature (T_g) of the polymer was 187.5°C. Details of these polymerization experiments are shown in Table 1.

Methacrylic anhydride (MAAn). Methacrylic acid was heated to reflux with acetic anhydride in the presence of hydroquinone (0.1 g) for 1 h. After distillation at 56°C/0.8 mm, the crude product was redistilled three times and the pure product was identified by GC analysis. Bp 45-46°C/0.5 mm.

Polymerization of methacrylic anhydride. The polymerizations of methacrylic anhydride were carried out with BPO as an initiator in solution or in bulk. Methacrylic anhydride (6 g) and 60 mg of BPO (1.0 wt% based on monomer) were dissolved in 50 mL of benzene. The solu-

TABLE 1. Cyclopolymerization of N-Phenyldimethacrylamide (PhDMA)[a]

PhDMA, g	AIBN, mg (wt%)	Benzene, mL	Yield, g (%)	η_{inh}[c]
5.0	12 (0.25)[b]	10	2.2 (44)	0.14
5.0	25 (0.5)	10	2.1 (42)	0.14
4.0	40 (1.0)	8	2.0 (50)	0.14
6.0[d]	9	-	3.5 (58)	0.16

[a] Polymerization temperature 50°C, polymerization time 4 d.
[b] Based on PhDMA.
[c] 0.5% in DMF, 30°C.
[d] Bulk polymerization (in the melt) at 90-95°C for 22 h.

tion was transferred to a 80-mL Pyrex polymerization tube and degassed by three freeze-thaw cycles (liquid nitrogen) before sealing it at 0.1 mm and placing it in a constant temperature bath at 80°C. After 12 h the tube was opened and the contents were poured into 400 mL of ether. Poly(methacrylic anhydride) was collected, washed, and dried overnight at 65°C and 0.1 mm; yield 5.8 g (97%); the inherent viscosity was 0.52 dL/g. The infrared spectrum showed characteristic peaks of the cycloanhydride at 1760 and 1805 cm^{-1} and a weak band of the carbon-carbon double bond at 1630 cm^{-1}. Details of these polymerization experiments are shown in Table 2.

TABLE 2. Cyclopolymerization of Methacrylic Anhydride (MAAn)[a]

MAAn, g	BPO, g (wt%)	Solvent, type and amount, mL	Yield, g (%)	η_{inh}[c]
6.0	60 (1.0)[b]	Benzene 50	5.8 (97)	0.52
1.0	100 (10)	Benzene 10	1.0 (100)	0.32
2.0	20 (1.0)	-	1.9 (95)	0.48
2.0	20 (1.0)	DMSO 20	0.7 (35)	1.98
Room temperature bulk polymerization			(87)	2.55

[a] Polymerization temperature 80°C, polymerization time 12 h.
[b] Based on MAAn.
[c] 0.5% in DMF, 30°C.

Room temperature bulk polymerization of methacrylic anhydride. Methacrylic anhydride (Pfaltz and Bauer, Inc.) (30 g) had been stored in a refrigerator over 4 years. It was found that most of the monomer had polymerized. After cooling in liquid nitrogen, the polymer plug was ground to a powder which was extracted in a Soxhlet extractor with diethyl ether for 3 d and dried overnight at 65°C and 0.1 mm. The yield of the polymer was 87%, and the polymer had an inherent viscosity of 2.55 dL/g in dimethylformamide.

Hydrolysis of polymethacrylic anhydride (PMAAn). Hydrolysis of poly(methacrylic anhydride) was carried out with base or in water. Poly(methacrylic anhydride) (1.0 g) was suspended in 50 mL of aqueous 2 N sodium hydroxide and heated to reflux. In a few minutes all the polymer had gone into solution and a clear solution was obtained; refluxing was continued for 5 h. The hot solution was filtered and acidified with concentrated hydrochloric acid. The polyacid which had precipitated was collected and dried overnight at 65°C and 0.1 mm; yield 0.68 g (65%).

Poly(methacrylic anhydride) (1.0 g) (from room temperature bulk polymerization, which was purified by dissolving the polymer in dimethylformamide and then precipitated by pouring the solution into water) was suspended in 150 mL of distilled water and allowed to reflux overnight. Most of the polymer had dissolved but refluxing was continued for an additional day. The solution was then filtered and the solution was evaporated to dryness. A clear film of poly(methacrylic acid) was obtained. After grinding the polymer to a fine powder, the polyacid was dried overnight at 65°C and 0.1 mm; yield 0.82 (80%).

Esterification of poly(methacrylic acid). Poly(methacrylic acid) (0.82 g) was suspended in 150 mL of benzene. Diazomethane (2.8 g) in ether (100 mL) was then added to this suspension. The mixture was stirred at room temperature for 2 d. The solvents were then evaporated under reduced pressure using a rotatory evaporator. To the residue, chloroform (50 mL) was added and the mixture was allowed to reflux for 2 h. The solution was filtered and poured into 400 mL of n-hexane which caused the poly(methyl methacrylate) to precipitate; it was collected by filtration and dried at 65°C and 0.1 mm; yield 0.51 g (50%). Details of the esterification experiments are shown in Table 3.

Polymerization of methyl methacrylate. Methyl methacrylate was polymerized in a vacuum-sealed polymerization tube in benzene solution using BPO as the radical initiator.

RESULTS AND DISCUSSION

The cyclopolymerization of selected methacrylic acid derivatives was investigated in order to evaluate the possibility that this method could be used for the preparation of intermediates that would ultimately lead to pure H-H PMMA. N-Phenyldimethacrylamide and

TABLE 3. Esterification of Poly(methacrylic Anhydride) (PMAAn)

Original PMAAn sample weight (g)	Poly(methacrylic acid)		Poly(methyl methacrylate)			Elemental analysis, Calc (%)	
	Yield (g)	Conversion (%)	Yield (g)	Conversion[a] (%)	GPC molecular weight	C, 59.98,	H, 8.05
1.0	0.68	61	0.26	33	73,000	C 59.75	H 8.03
1.0	0.70	63	0.32	39	88,000	C 60.08	H 8.31
1.0	0.82	73	0.51	53	378,000	C 60.75	H 8.35

[a] Based on poly(methacrylic acid).

methacrylic anhydride were cyclopolymerized, and experiments were carried out to hydrolyze and esterify the cyclopolymers to MMA polymers.

Cyclopolymerization of N-phenyldimethacrylamide with AIBN as the initiator yielded, in about 50% conversion, cyclopolymers with a relatively low inherent viscosity of about 0.15 gL/g. The polymerization was carried out in benzene solution and also in the melt with approximately the same results (Table 1). The high resolution ^{1}H-NMR spectrum (250 MHz) showed a spectrum of poly(N-phenylmethacrylamide) (PPhDMA) which had the typical ^{1}H-NMR chemical shift values of a cyclopolymer (Fig. 1). More information was obtained by investigation of the ^{13}C-NMR spectrum of PPhDMA (Fig. 2). It had typical ^{13}C-NMR chemical shift values of the cyclopolymers as shown in Table 4. Characteristic are the chemical shift values at 50.6 ppm, typical for the quarternary carbon atom of five-membered ring cyclopolymers of methacrylic acid derivatives. Also observed in this spectrum were chemical shift values at 41.0 ppm, typical for quarternary carbon atoms of six-membered rings. By careful studies of the spectra obtained under various and optimal conditions, quantitative evaluation showed that the six-membered ring (the glutaramide structure) was present in approximately 6% of the total.

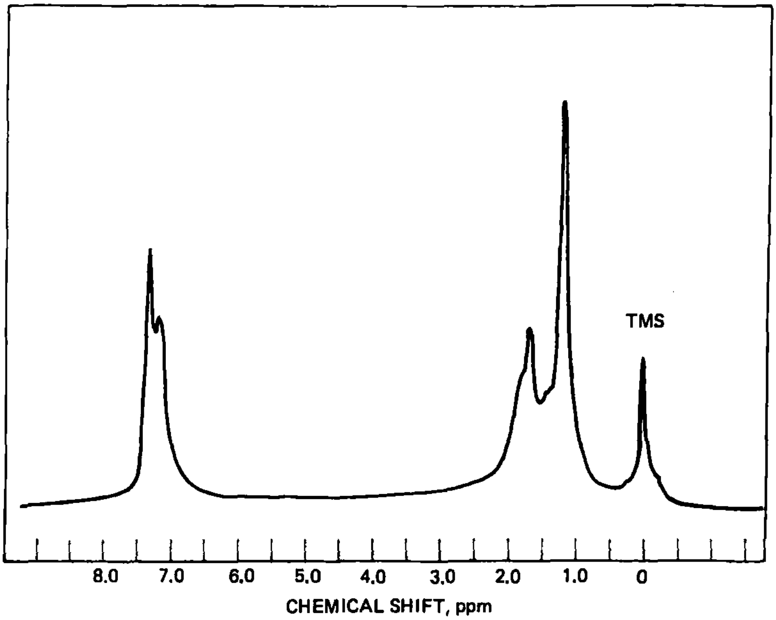


FIG. 1. High resolution ^{1}H-NMR spectrum of poly(N-phenyldimethacrylamide) (PPhDMA) (250 MHz).

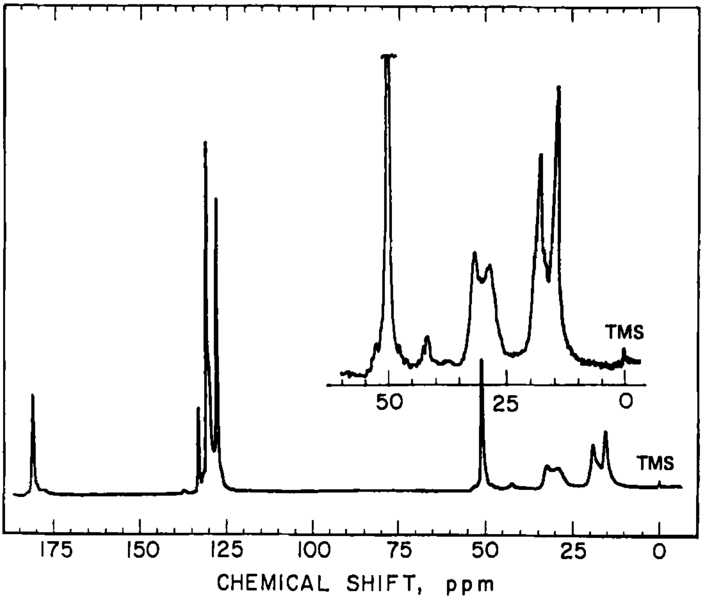


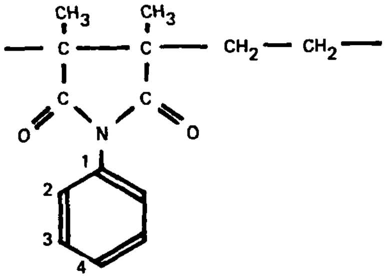
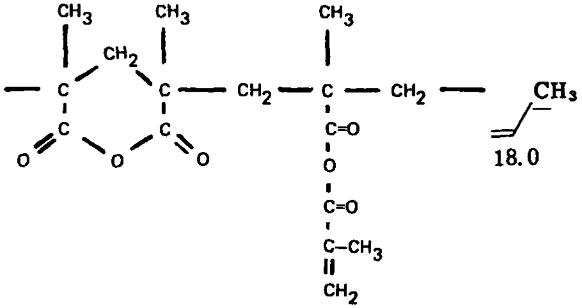
FIG. 2. ^{13}C-NMR spectrum of poly(N-phenyldimethacrylamide) (PPhDMA).

Methyl chemical shifts at 18.6 ppm and methylene chemical shifts at 32.3 ppm confirmed the quantitative evaluation of a six-membered cyclopolymer structure present in the polymer. It is well known that six-membered structures, as well as open ring structures, lead to head-to-tail structures in PMMA after successful hydrolysis and esterification to the methyl ester. As a consequence, this route, the cyclopolymerization of methacrylanilides, clearly did not give the desirable starting material or intermediates in sufficiently pure quantity to pursue further the attempted preparation of purely H-H PMMA by cyclopolymerization.

Furthermore, extensive efforts have been undertaken to hydrolyze poly(N-phenyldimethacrylamide) to the H-H poly(methacrylic acid). The hydrolysis conditions included normal hydrolysis in aqueous sodium hydroxide or potassium hydroxide in dilute solution and also in concentrated solution as far as 4 N. It also included hydrolysis in the presence of various amounts of methanol or 1,4-dioxane. In all cases the starting material was recovered unchanged.

It is well known that phthalimide derivatives are used as protective groups in peptide synthesis or at least in the formation of peptide links during peptide synthesis. The traditional way of removal of the phthalic acid group is the treatment of the phthalimide derivative with hydrazine. We have also adopted the hydrazinolysis method

TABLE 4. ^{13}C-NMR Chemical Shift Data of Cyclopolymers of Methacrylic Acid Derivatives

Cyclopolymer	Chemical shift (δ ppm)					$-C_6H_5$			
	$-CH_3$	$-CH_2-$	$=CH_2$	$-\overset{\vert}{\underset{\vert}{C}}-$	$\overset{\vert}{\underset{\vert}{C}}=O$	^1C	^2C	^3C	^4C
Poly(N-phenyldimethacrylamide) 	15.0, 18.6	28.9, 32.3		50.6 (in 5-membered ring) 41.0 (in 6-membered ring)	180.1	131.8	126.3	129.2	128.5
Poly(methacrylic anhydride) 	23.1, 24.8	45.8, 48.5	124.8	42.6	171.8				

for the possible destruction of the succinimide group in poly(N-phenyldimethacrylamide). Anhydrous hydrazine and hydrazine monohydrate have been used to treat poly(N-phenyldimethacrylamide) for short periods (even periods as long as a week) without success. As a consequence, the route to H-H PMMA via poly(N-phenyldimethacrylamide) was abandoned. It has been claimed previously, and this now appears to be a fact, that hydrolysis of the five-membered succinimide ring of this cyclopolymer of methacrylimide derivatives is very difficult, for all our methods have failed.

In parallel experiments, the cyclopolymerization of methacrylic anhydride has also been carried out under various conditions in order (a) to establish what kind of units in the polymer structures were obtained by this cyclopolymerization; (b) to evaluate the polymers structure for the cyclopolymers with five-membered rings, six-membered rings, and open chain material. It should again be pointed out that only five-membered derivatives would give, upon hydrolysis and esterification, the desired H-H PMMA; (c) to develop methods for quantitative esterification of the polymeric cyclic anhydrides to the poly(methyl methacrylates).

Cyclopolymerization of MAAn was carried out in benzene solution in DMSO and in bulk. Benzene solution and bulk polymerization gave the polymer in high to nearly 100% yield with an inherent viscosity of 0.3 to 0.5 dL/g while polymerizations in DMSO as the solvent gave cyclopolymers of an inherent viscosity of nearly 2 dL/g (Table 2).

From previous work we had a sample of MAAn which had polymerized over years in the bulk and at room temperature. This sample was extremely difficult to dissolve but DMF (directly from the bottle, but not purified DMF) was able to dissolve the sample completely. It is believed that the insolubility of the sample was caused by the possible cross-linking reactions caused by polymerizations whose propagation had left, on occasion, one monomer unit unpolymerized. Under bulk polymerizations conditions at room temperature, the second double bond of the monomer also took part in the polymerization of a different polymer chain, consequently causing cross-linking. These cross-links were, however, weak links and were probably hydrolyzed by some water which is always an impurity in DMF. Once the polymer had been dissolved in DMF and reprecipitated, it was readily redissolved although it was of high molecular weight (η_{inh} 2.5 dL/g) and a styrene GPC viscosity of 378,000 (Table 2).

The infrared spectrum of the various preparations of PMAAn prepared with BPO as the initiator or by room temperature bulk polymerization were superimposable (Fig. 3). The ^{1}H-NMR spectrum of PMAAn prepared with BPO as the initiator showed ^{1}H-NMR peaks typical for the methyl-, methine groups and the free double-bonded methylene groups of the noncyclized products. There was also some broad resonance between 3 and 3.5 ppm whose exact structure has not been determined (Fig. 4).

The ^{13}C-NMR spectrum of PMAAn from MAAn with BPO as the initiator also shows the typical chemical shift values expected from

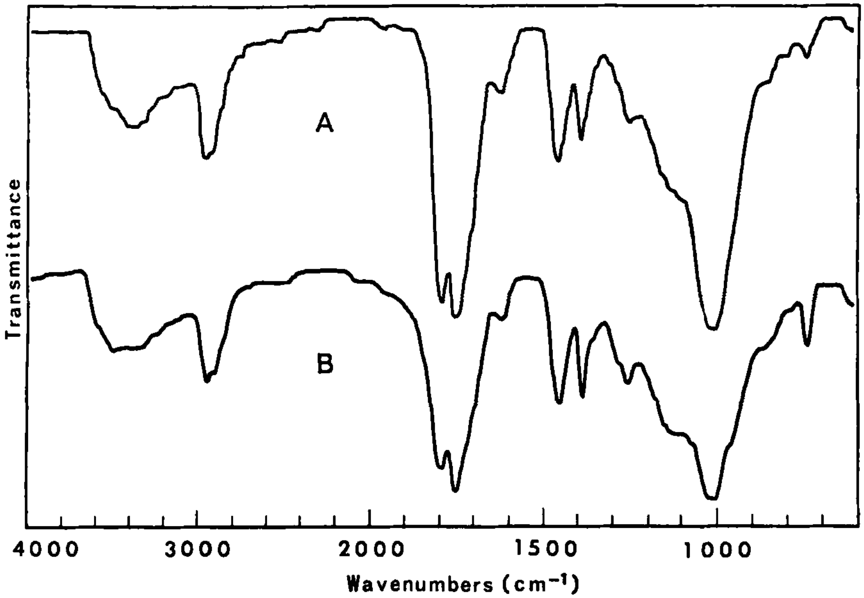


FIG. 3. Infrared spectra of poly(methacrylic anhydride) (PMAAn). A: From MAAn with BPO. B: From room temperature bulk polymerization.

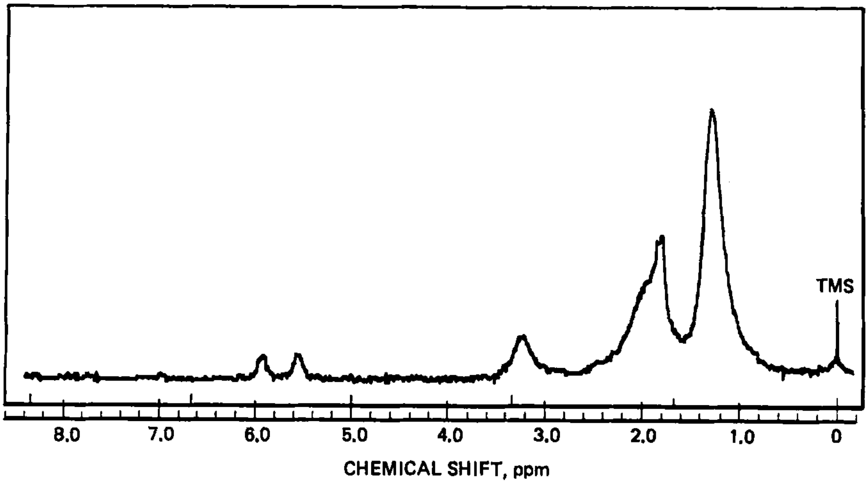


FIG. 4. ^{1}H-NMR spectrum of PMAAn from MAAn with BPO.

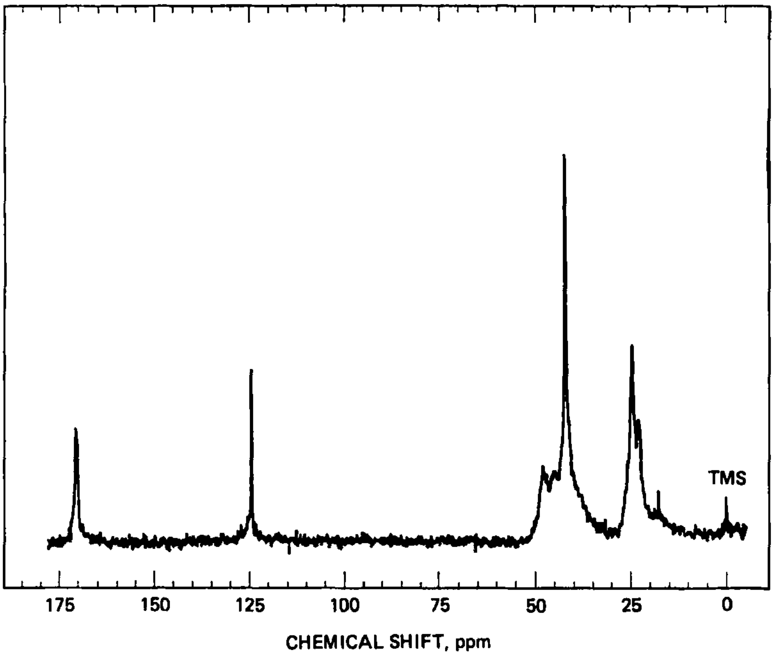


FIG. 5. ^{13}C-NMR spectrum of PMAAn from MAAn with BPO.

the six-membered ring structure (Fig. 5), particularly the quartenary carbon atom at 42.6 ppm. In addition, the methyl groups showed at 24.8 ppm and the methylene groups at 48.5 ppm. The methyl group attached to the free vinyl group of the uncyclized material was found in small amounts at 18.0 ppm.

PMAAn obtained from solution polymerization or from room temperature bulk polymerization was esterified quantitatively with diazomethane to PMMA and was compared with a polymer obtained from MMA with BPO as the initiator (Table 3). The three infrared spectra are superimposable as shown in Fig. 6, indicating that both PMAAn, the one from solution polymerization and the one from room temperature bulk polymerization, had either cyclopolymerized entirely to six-membered rings or to six-membered rings with a certain percentage of open chain units in the polymer chain which on esterification gave H-T PMMA.

Figure 7 shows that the ^{1}H-NMR spectra of the three samples of H-T PMMA were also very similar but had subtle differences in the 1.0 ppm range. These would be expected from slight differences in the stereochemistry of the H-T PMMA caused by variations in isotactic, heterotactic, and syndiotactic placements of the methyl group (Fig. 8B). Similar results were observed upon inspecting the ^{13}C-NMR spectra

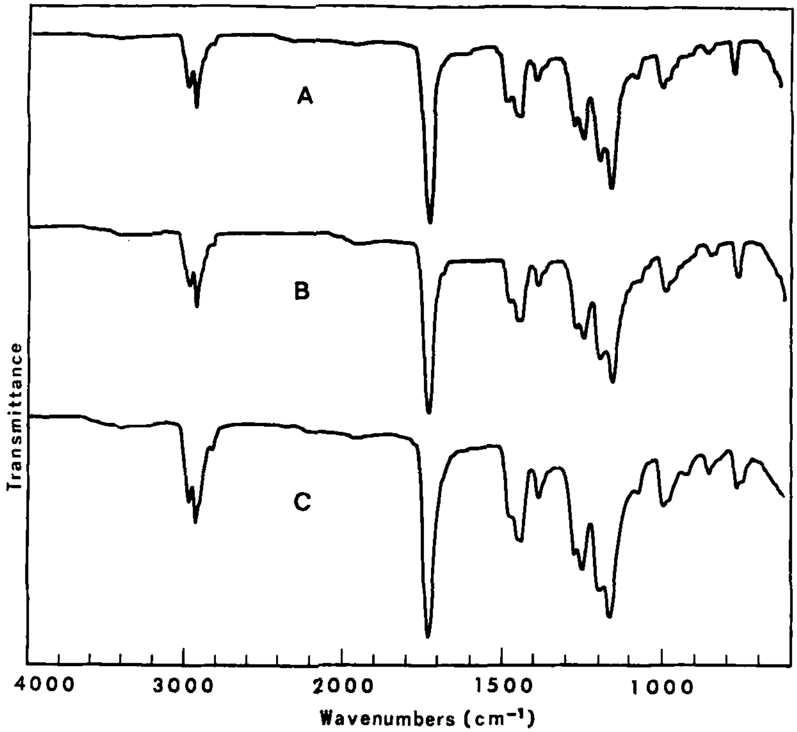


FIG. 6. Infrared spectra of PMMA. A: From polymerization of MMA with BPO as initiator. B: From esterification of PMAAn (solution polymerization) with diazomethane. C: From esterification of PMAAn (room temperature bulk polymerization) with diazomethane.

of the three types of PMMA's (Table 5, Fig. 8). Although differences were found in the methylene quartenary carbon atom and in the carbonyl region, the most important and identifiable differences were in the ^{13}C-NMR chemical shift data of the methyl group. The chemical shift value for the syndiotactic placement of the methyl group is at 16.6 ppm, that of the heterotactic placement at 18.8, and that of the isotactic at 21.0 ppm. The polymer obtained from radical polymerization of MMA with BPO as the initiator showed a predominance of syndiotactic placement at 16.6 ppm with a somewhat lesser intensity at 18.8 ppm of the heterotactic placement. There is essentially no isotactic placement observable in spectrum Fig. 8(A).

PMMA obtained by esterification of PMAAn (solution polymerization) shows that in this case the heterotactic portion is the predominant structural unit with a small amount of isotactic placement noticeable. PMMA obtained by esterification of PMAAn (room temperature bulk

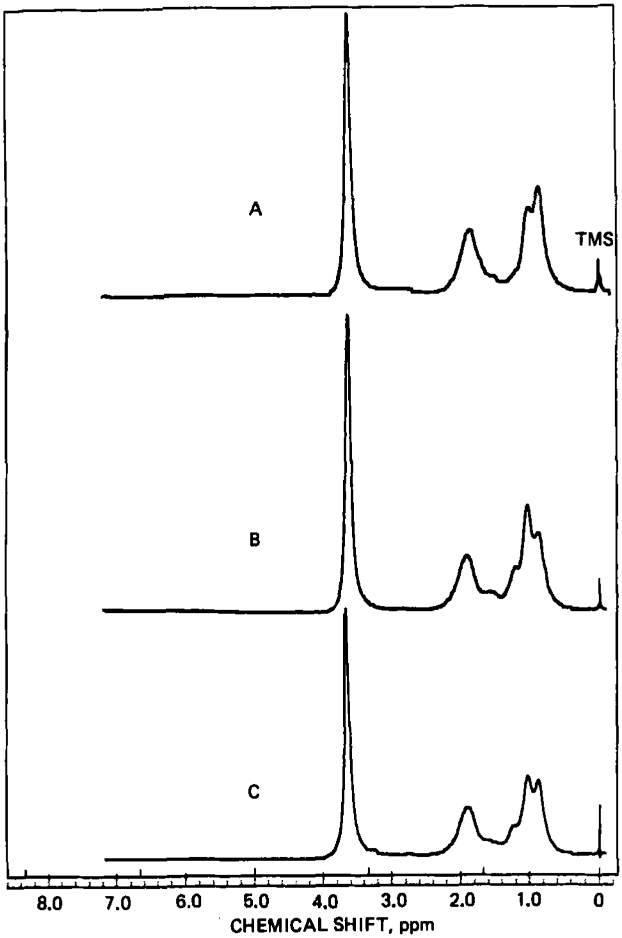
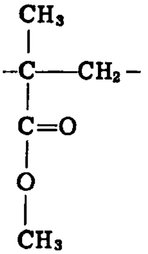


FIG. 7. ^{1}H-NMR spectra of PMMA. A: From polymerization of MMA with BPO initiator. B: From esterification of PMAAn (solution polymerization) with diazomethane. C: From esterification or PMAAn (room temperature bulk polymerization) with diazomethane.

polymerization) (Fig. 8C) shows that in this case of high molecular weight material, the syndiotactic material is the predominant structure followed by heterotactic with a small amount of clearly identifiable isotactic placement in the polymer structure.

In Table 3 are shown the reaction conditions and the results of the esterification of PMAAn. Hydrolysis, after careful work-up, gave 60-70% polymeric methacrylic acid, and subsequent esterification gave between 35 and 55% conversion, essentially 100% esterified PMMA.

TABLE 5. ^{13}C-NMR Chemical Shift Data of Polymeric Methyl Esters of Methacrylic Acid Derivatives

PMMA	Chemical shift (δ ppm)				
	$-CH_3$	$-CH_2-$	$-\overset{\vert}{\underset{\vert}{C}}-$	$-OCH_3$	$\overset{\vert}{\underset{\vert}{C}}=O$
 $-\overset{CH_3}{\underset{C=O-O-CH_3}{C}}-CH_2-$	16.6 rr	54.5	44.6 rr	51.8	177.0 rm
	18.8 rm		45.0 rm		177.8 rr
	21.0 mm		45.6 mm		

The polymerization of PMMA with BPO or the cyclopolymerization of MAAn followed by esterification gave molecular weights of H-T PMMA in the range of 70,000-90,000 (GPC molecular weight), while the bulk polymerized PMAAn gave, after esterification, a PMMA of nearly 400,000 molecular weight.

On the basis of our experiments we conclude that cyclopolymerization of methacrylic acid derivatives followed by hydrolysis and esterification is not a feasible route for the preparation of pure H-H PMMA. Cyclopolymerization, even under most favorable conditions, namely by the use of dimethacrylamide derivatives for cyclopolymerization, gave cyclopolymers which contained at the very best 94% five-membered units in the polymer chain. Furthermore, these polymers cannot be hydrolyzed to the free acid and consequently not esterified to the polymeric esters. On the other hand, methacrylic anhydride can be cyclopolymerized but only and entirely to a polymer that contains only six-membered rings and some noncyclized structures in the polymer chain. These PMAAn samples can be hydrolyzed to the polymeric acid and then esterified quantitatively with diazomethane to PMMA (Table 5).

All three samples of PMMA studied show great similarities in their structure but some differences in their stereochemistry. PMMA polymerized with BPO as the radical initiator shows predominantly syndiotactic-type placements with almost equal amounts of heterotactic placement but with very small amounts, if any, of isotactic placement. PMMA obtained by BPO polymerization (solution polymerization), followed by hydrolysis and quantitative esterification with diazomethane, gave structures that have predominantly heterotactic stereochemistry with substantial amounts of syndiotactic and a noticeable

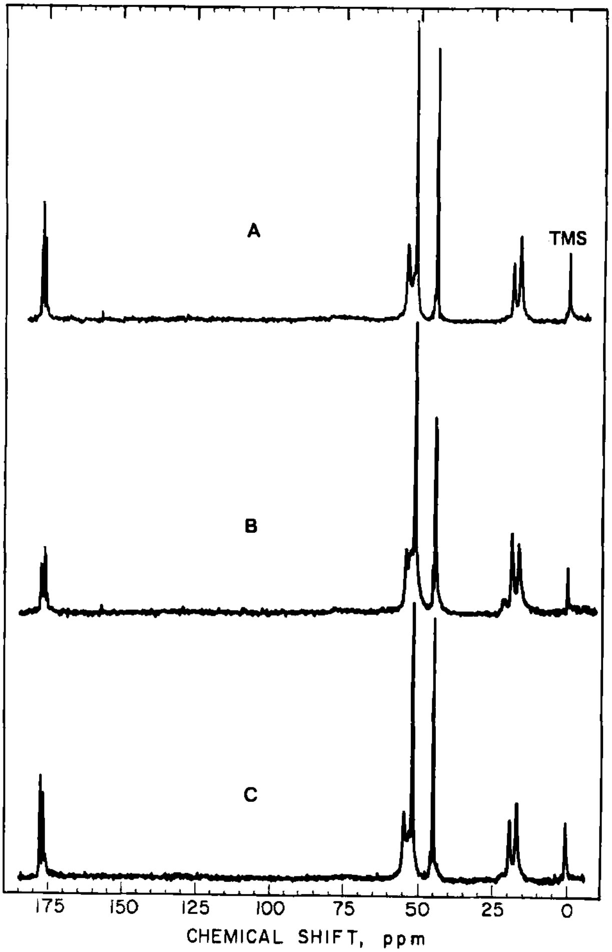


FIG. 8. ^{13}C-NMR spectra of PMMA. A: From polymerization of MMA with BPO as initiator. B: From esterification of PMAAn (solution polymerization) with diazomethane. C: From esterification of PMAAn (room temperature bulk polymerization) with diazomethane.

amount of isotactic triads present. High molecular weight PMAAn obtained by room temperature bulk polymerization of MAAn after hydrolysis and esterification with diazomethane gave PMMA which had syndiotactic and heterotactic units with noticeable amounts of isotactic placement.

The search for alternate routes for the preparation of pure H-H PMMA will be continued.

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