

Cyclopolymerization of Dodecanidiol Dimethacrylate and Identification of Polymer Structure

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SYNOPSIS

Dodecanidiol dimethacrylate (DDMA) was polymerized by a cyclization mechanism in low monomer concentration (0.075–0.5 mol/L) and high AIBN concentration ($0.44\text{--}1.76 \times 10^{-2}$ mol/L). The linear soluble polymer was formed even if the conversion of DDMA was as high as 25.6%. The glass transition temperature of cyclized polyDDMA (PDDMA) is about 4.5°C, which is 65°C higher than its homolog—poly(dodecyl methacrylate). The structure of the polymer was established by infrared and ¹H- and ¹³C-NMR spectroscopy. The head-to-tail contents in cyclized PDDMA, i.e., the formation of a 20-membered ring, is predominant compared with those of head-to-head contents of a 19-membered ring. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Dimethacrylate (DMA) and its polymer have been proven to be very useful in a wide variety of biomedical applications^{1,2} and microelectronics research.³ However, its strong polymerization shrinkage may introduce trouble for the application of a direct filling material.

To improve the shrinkage properties of DMA, a series of DMA monomers with a long methylene chain was synthesized. Our object was to explore the relationship between shrinkage behavior and the methylene chain length of DMAs.

However, in the radical polymerization of DMA with a long methylene chain, the polymerization of all these monomers in benzene was conducted by a cyclopolymerization mechanism in a low monomer concentration and high initiator concentration. The linear soluble polymer was formed even if the conversion of dodecanidiol dimethacrylate (DDMA) was as high as 26.5%. Therefore, such questions, e.g., of how large the ring size is in the polymer chain and what is the addition mode for a growing chain radical to the monomer are certainly very interesting for us.

It is well known that the head-to-tail (ht) addition for the attack of a growing chain radical on a monomer is predominant compared with other types of addition modes such as head-to-head (hh) and tail-to-tail (tt) in the radical polymerization of vinyl monomers, thus, forming the polymer mainly of ht structure. This fact has been explained by some qualitative considerations of resonance stability and steric factors leading to the intermediate formation of a more stable free radical.⁴ Most of the difunctional monomers reported have been assumed to be formed of a 5- or 6-membered ring in the polymerization in terms of the expected thermodynamic stability.^{5,6} There are limited articles in which the formation of a large ring structure in the polymerization has been reported.

In the research of cyclopolymerization of diallyl phthalate, a preferential 11-membered ring, i.e., the product of ht addition, was reported by Matsumoto et al.⁷ which is irrespective of the polymerization temperature, although hh addition has been enhanced with an increase in temperature in common radical polymerization of vinyl monomers.⁸

In our polymerization system, we also found that the ht addition mode is predominant compared with tt via structure analysis of the cyclized poly(DDMA) (PDDMA), which means that the occupied main content of the polymer chains is 20-membered rings.

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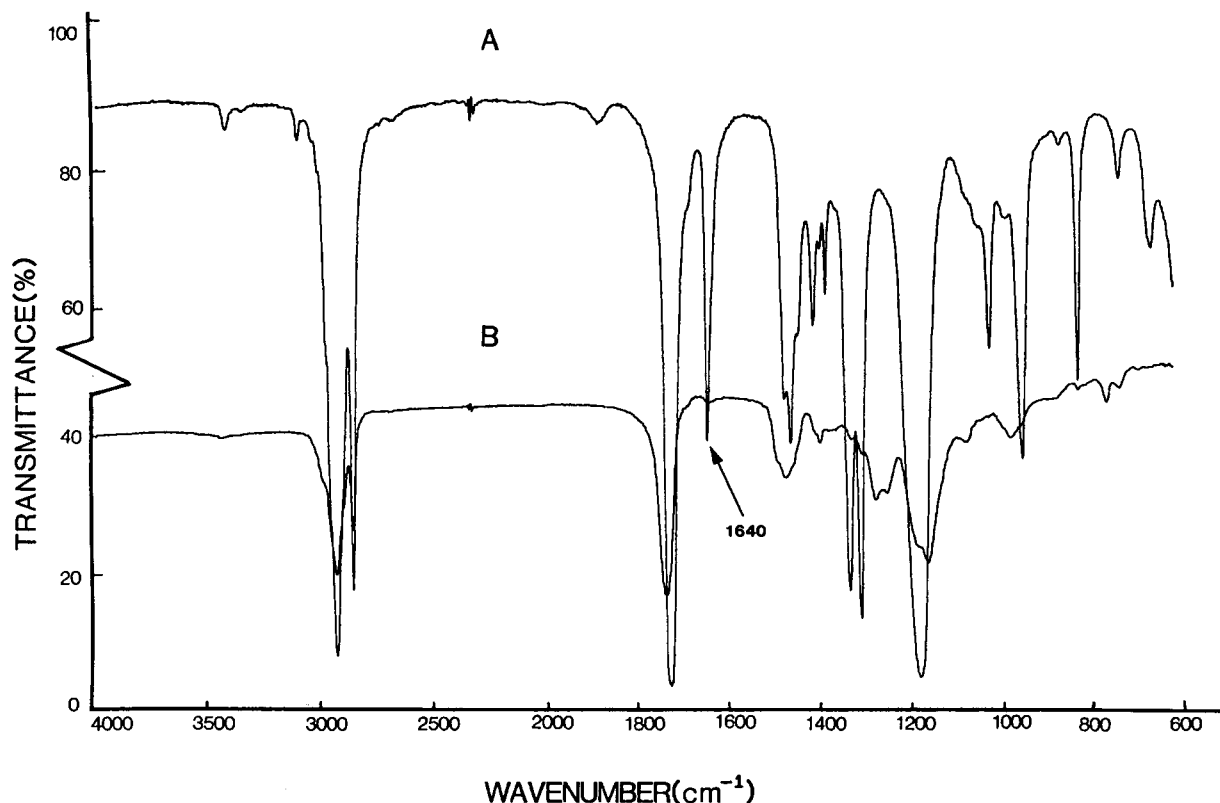


Figure 1 IR spectra of DDMA (A) before and (B) after polymerization. Polymerization conditions: $[I]$: 1.76×10^{-2} mol/L; $[M]_0 = 0.075$ mol/L; T : 60°C , 10 min.

Similar results could be derived from other DMA monomers with long methylene chains such as tridecanediol dimethacrylate, pentadecanediol dimethacrylate, hexadecanediol dimethacrylate, and eicosadecanediol dimethacrylate. We will report on them in forthcoming articles.

EXPERIMENTAL

Materials

1,12-Dodecanediol dimethacrylate was obtained from Esschem Co., USA, which was purified by passing the monomer diluted with twice the volume of *n*-pentane through a column chromatograph (diameter: 50 mm). The latter was composed of two layers: The upper is 30 cm of basic alumina (W_{200} Woelm pharma) and the lower is 20 cm of silica gel (Kjesel gel 100, 70–230 mesh, Merck). The purity of DDMA was checked by high-performance liquid chromatography (HPLC); the content is more than 98%. Azobisisobutylnitrile (AIBN) was recrystallized twice by ethanol (mp: $104\text{--}105^\circ\text{C}$). 2,3-Dimethyl maleic anhydride (DMMAH) (from Aldrich) was recrystallized from petroleum ether before use.

Ethylene was supplied by Shanghai Jin Shan Petroleum Chemical Factory.

Polymerization Procedure

DDMA was polymerized in benzene at 60°C with AIBN as an initiator in an argon atmosphere. The polymerization was carried out in an ampule by the freeze-thaw method. The product was obtained by pouring the liquefied contents of the ampule into methanol saturated by O_2 for a specified time. The monomer and initiator concentrations are in the range of $0.075\text{--}0.5$ mol/L and $0.44\text{--}1.76 \times 10^{-2}$ mol/L, respectively.

The polymer could be purified by dissolution in dichloromethane and reprecipitation into methanol. The purified product is a white powder and quite soluble in common solvents as aromatic and chloro-substituted hydrocarbons and tetrahydrofuran.

Measurement of Contents of Residual Double Bond

Residual double bonds in the polymer were calculated using the intensity of infrared absorbance at 1640 cm^{-1} of $\text{C}=\text{C}$; the formula is as follows:⁹

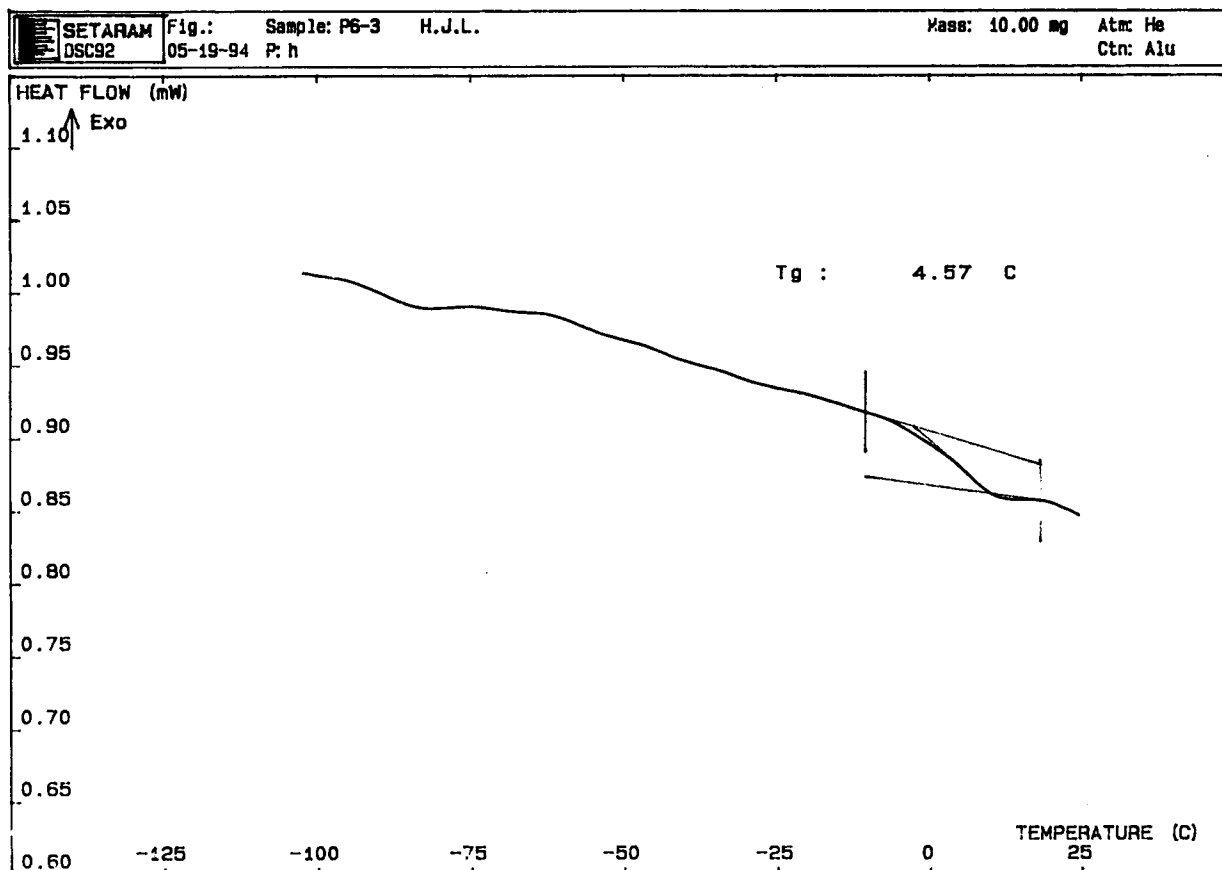


Figure 2 DSC diagram of PDDMA (\bar{M}_n : 1.3×10^4).

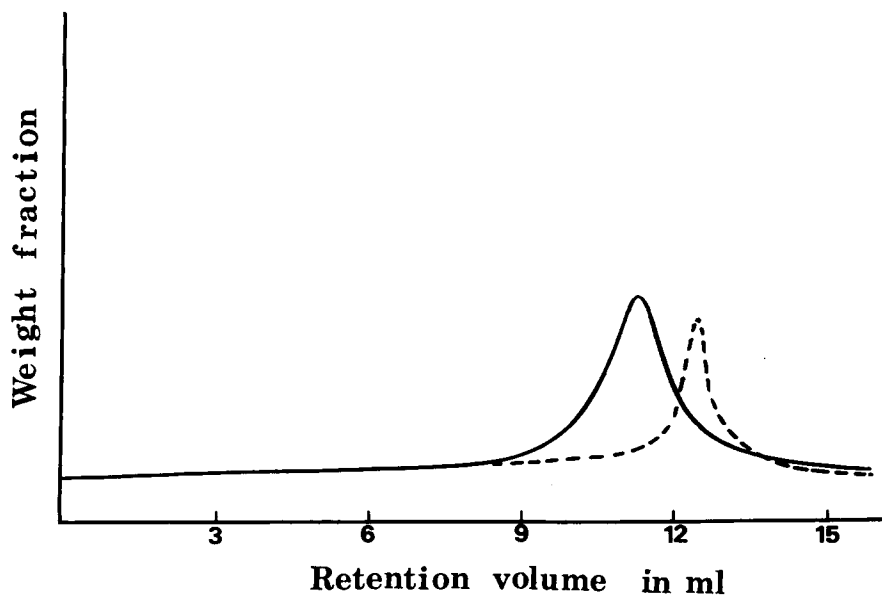


Figure 3 GPC measurement of PDDMA: (---) $[M]_0 = 0.05$ ml/L, \bar{M}_n : 1.3×10^4 , \bar{M}_w/\bar{M}_n : 1.34; (—) $[M]_0 = 0.52$ ml/L, \bar{M}_n : 5.6×10^4 , \bar{M}_w/\bar{M}_n : 2.59.

Table I Effect of Concentration of Monomer and Polymerization Time on f_c

Run ^a No.	[M] (mol/L)	Time (Min)	Conversion (%)	f_c		
				a	b	c
p 1-1	0.075	10	0.9	0.91	0.93	0.92
p 1-2		15	3.7	0.92	0.93	0.92
p 1-3		20	8.3	0.93	0.94	0.93
p 1-4		25	10.4	0.95	0.93	0.94
p 1-5		30	13.9	0.95	0.95	0.95
p 2-1	0.1	10	1.7	0.90	0.93	0.90
p 2-2		15	8.2	0.90	0.94	0.89
p 2-3		20	9.5	0.91	0.93	0.91
p 2-4		25	11.9	0.92	0.93	0.92
p 2-5		30	14.7	0.92	0.94	0.93
p 3-1	0.15	10	4.7	0.90	0.92	0.89
p 3-2		15	11.4	0.91	0.93	0.91
p 3-3		20	15.7	0.91	0.92	0.90
p 3-4		25	17.4	0.91	0.92	0.91
p 3-5		30	19.3	0.92	0.93	0.92
p 4-1	0.20	10	8.0	0.88	0.91	0.89
p 4-2		15	10.6	0.89	0.90	0.89
p 4-3		20	15.8	0.89	0.92	0.89
p 4-4		25	19.3	0.90	0.92	0.89
p 4-5		30	25.6	0.91	0.91	0.90
p 5	0.52	10	23.0	0.86	0.88	0.85

^a [I]: 1.76×10^{-2} mol/L; temperature: 60°C; solvent: benzene; a: bromination; b: ¹H-NMR; c: IR.

$$f_c = \frac{R_c}{R_c + R_p} = \frac{A_p - A_r}{A_p} = 1 - \frac{MA_r}{\xi cl} \quad (1)$$

where f_c is the fraction of cyclized units; R_c and R_p , the cyclization and propagation rate, respectively; A_p , the absorbance of an ideal noncyclized polymer; A_r , the absorbance of the residual double bond in the polymer sample; M , the weight of repeating unit of the polymer with a pendant double bond of methacrylate in g/mol; ξ , the extinguishing coefficient of

DDMA—the value is $6.61 \text{ mol mm}^{-1} \text{ L}^{-1}$; c , the concentration of the polymer sample in g/L; and l , the thickness of the sample cells in mm. The extent of cyclization was also determined by bromization and ¹H-NMR according to the variation of the area of absorption due to vinyl proton at 5.7 and 6.3 ppm. For the bromization, after the polymer was reacted with excess bromine in chloroform at room temperature for 8 h, the content of bromine reacted was determined by the Ota method.¹⁰

Table II Effect of Polymerization Temperature on f_c

Run ^a No.	Temperature (°C)	Conversion (%)	f_c		
			a	b	c
p 6-1	50	4.7	0.90	0.91	0.91
p 6-2	65	12.4	0.91	0.91	0.91
p 6-3	70	15.6	0.92	0.92	0.91
p 6-4	80	20.0	0.93	0.94	0.92

^a [I]: 1.76×10^{-2} mol/L; [M]: 0.1 mol/L; time: 20 min. See footnote to Table I for a, b, and c meanings.

Synthesis of Model Compounds of Poly(methyl methacrylate) with Head-to-Head and Head-to-Tail Structures

Poly(methyl methacrylate) (PMMA) consisting entirely of head-to-head placements was prepared by copolymerization of ethylene and 2,3-dimethyl maleic anhydride by the method of Otsu,¹¹ then hydrolyzed with methanol in refluxing conditions and methylated with diazomethane in THF at room temperature; ht PMMA was derived from common PMMA obtained by radical polymerization of MMA.

Table III Effect of Concentration of Initiator of f_c

Run ^a No.	[I] ($\times 10^{-2}$ mol/L)	Conversion (%)	f_c		
			a	b	c
p 7-1	1.10	8.3	0.91	0.91	0.90
p 7-2	0.88	7.8	0.90	0.92	0.90
p 7-3	0.66	7.0	0.89	0.91	0.89
p 7-4	0.44	6.1	0.89	0.90	0.90

^a [M]: 0.1 mol/L; temperature: 60°C; time: 20 min. See footnote to Table I for a, b, and c meanings.

Measurements of Cyclized Structure in PDDMA

The cyclized PDDMA was hydrolyzed with concentrated sulfuric acid¹² and methylated with diazomethane in diethyl ether¹³ to form PMMA. The ht and hh contents of cyclized PDDMA were determined by comparing its ¹³C-NMR spectra with the model compounds.

Instruments

IR spectra were recorded on Perkin-Elmer 983G; ¹H- and ¹³C-NMR spectra were performed on Bruker MSL-300 (300 MHz) spectrometer using deuteriochloroform as a solvent and tetramethylsilane as an internal reference. DSC studies were conducted with a SETARAM DSC 92 in a helium atmosphere at a heating rate of 10°C/min. The measurements

of molecular weight and molecular weight distribution of PDDMA were completed with a Shimadzu LC-3A liquid chromatograph under the following conditions: column length, 1.2 m; filler, crosslinked polystyrene gel (1250 mesh) (from Ji Lin University of China); injection volume of sample solution, 0.1 mL (concentration: 0.1 g/100 mL); solvent and eluent, tetrahydrofuran; flow rate, 1.2 mL/min; pump pressure, 80 kg/cm² (7.85×10^6 Pa); and detecting wavelength, 254 nm. The resulting GPC curves were then analyzed by using the calibration curve obtained with standard samples of monodispersed polystyrene.

RESULTS AND DISCUSSION

Evidence of Cyclopolymerization of DDMA

Figure 1 is the IR spectra of DDMA before (A) and after polymerization (B). The 1640 cm⁻¹ assigned as the stretching vibration of C=C nearly disappeared after polymerization. We think that it is impossible for them to be consumed in the crosslinking process due to their great solubility in the common organic solvents. The right way to consume the double bonds is by cyclization.

Figure 2 is the DSC diagram of PDDMA. Its T_g is about 4.5°C, which is 70°C higher than its homolog—poly(dodecyl methacrylate)^{14,15} (its T_g is about -65°C). The higher T_g of PDDMA is contributed to the formation of large-size rings in the

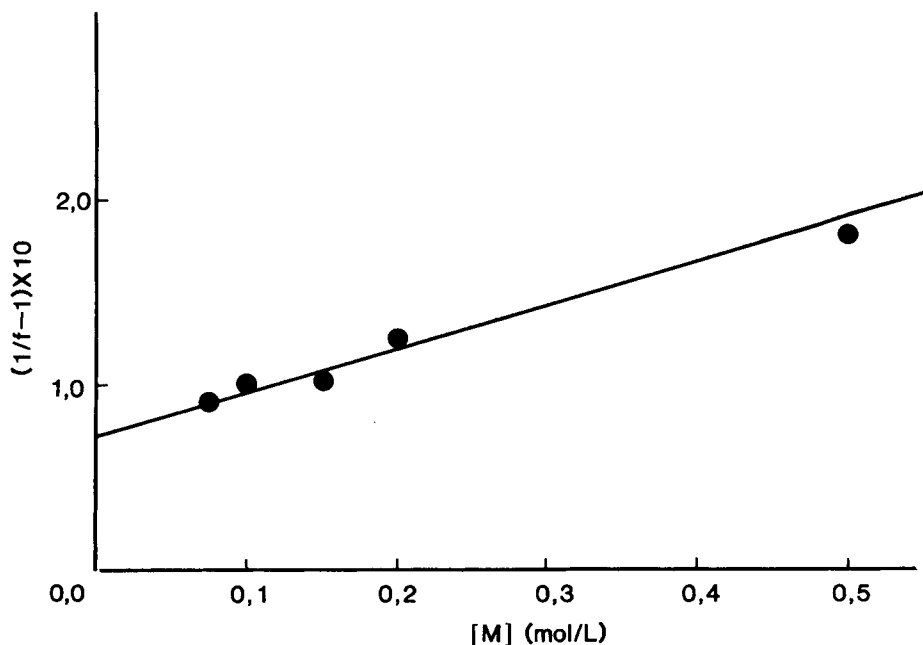


Figure 4 Plot of $(1/f_c - 1)$ vs. $[M]$. [I]: 1.76×10^{-2} mol/L; T : 60°C, 20 min.

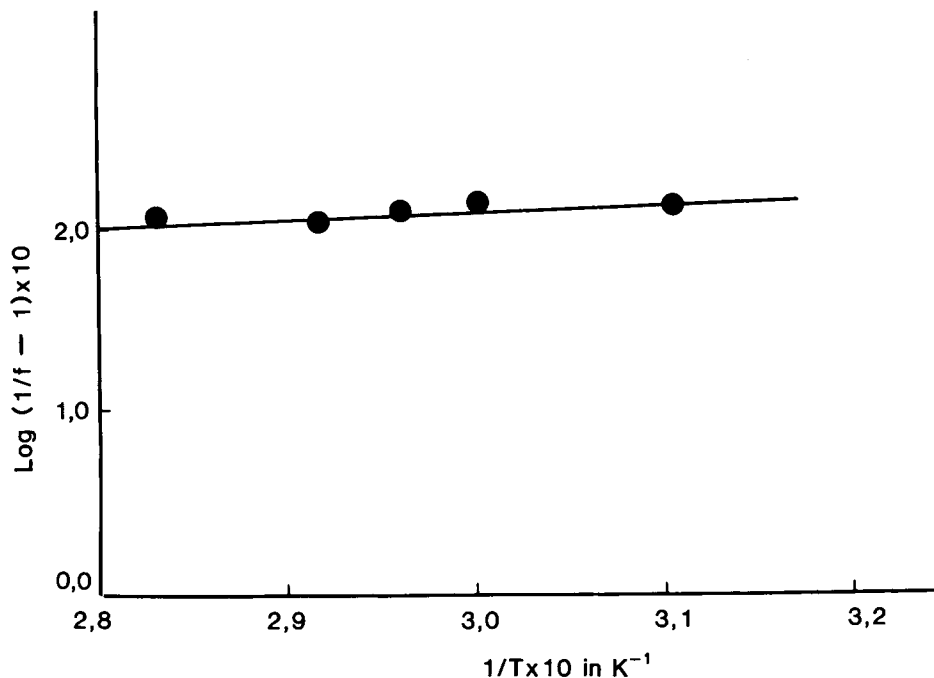


Figure 5 Plot of $(1/f_c - 1)$ vs. $1/T$. $[I]: 1.76 \times 10^{-2}$ mol/L; $[M]: 0.1$ mol, 20 min.

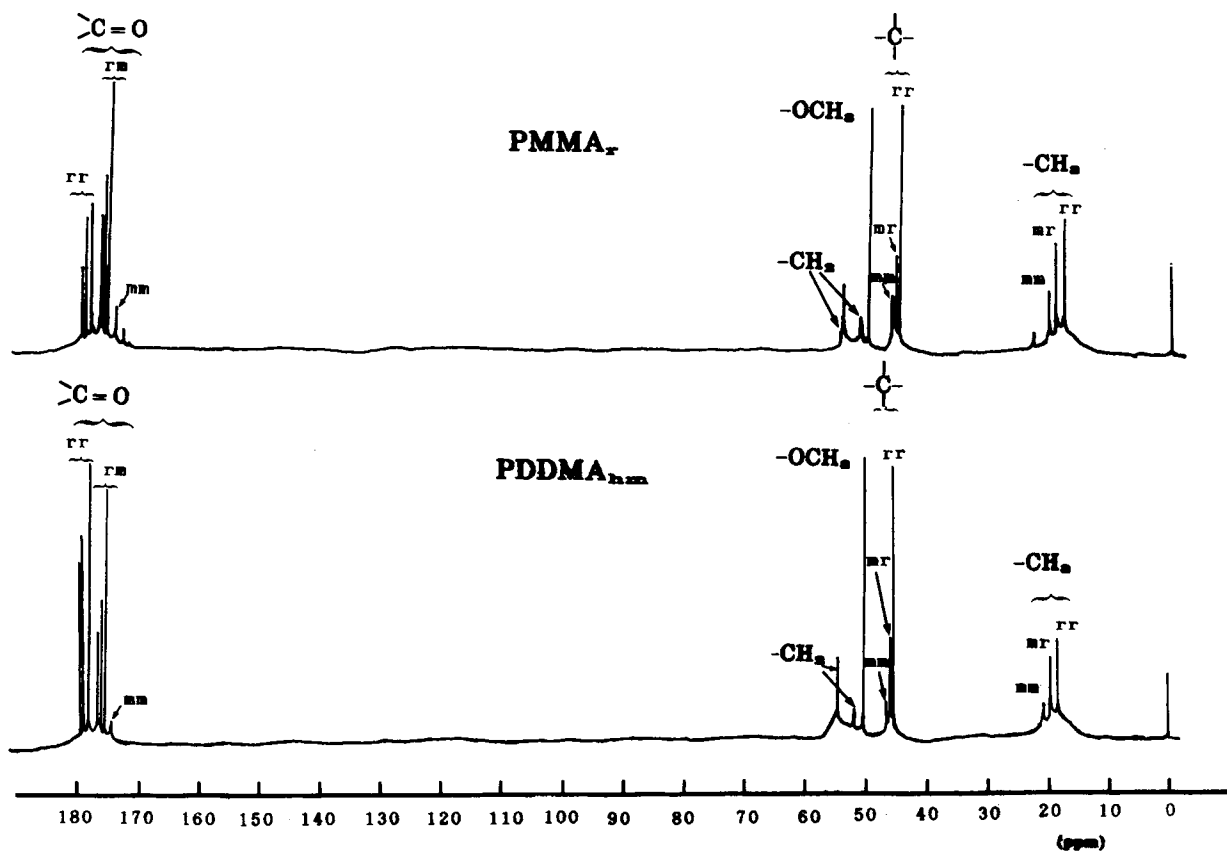


Figure 6 ^{13}C -NMR spectra of hydrolyzed and then methylated $\text{PDDMA}_{h,m}$ and PMMA_r , derived from the radical polymerization in deuteriochloroform.

Table IV ^{13}C Chemical Shifts of PDDMA and PMMA

Sample	^{13}C Chemical Shift (ppm)					
	C=O	—CH ₂ —	—C— 	αCH_3	—OCH ₃	
PDDMA ^a	<i>r</i> ^a <i>r</i>	179.0	54.7	<i>m</i> ^b <i>m</i> 46.1	<i>mm</i> 21.8	52.0
		178.6	53.8	<i>mr</i> 45.2	<i>mr</i> 19.1	
		177.9		<i>rr</i> 44.9	<i>rr</i> 17.0	
	<i>rm</i>	177.1				
		176.5				
		175.9				
	<i>mm</i>	175.8				
PMMA ^b	<i>rr</i>	178.8	54.3	<i>mm</i> 44.7	<i>mm</i> 21.1	50.3
		178.3		<i>mr</i> 44.2	<i>mr</i> 17.4	
		177.7		<i>rr</i> 43.4	<i>rr</i> 16.6	
	<i>rm</i>	177.0				
		176.8				
		176.4				
	<i>mm</i>	175.9				

a: raceme; *b*: mesomer.

^a Sample was prepared by hydrolysis and methylation of PDDMA.

^b Sample was prepared by radical polymerization of MMA.

polymerization which make the chain movement difficult.

Figure 3 is the GPC measuring results of PDDMA. Its molecular weight is in the range of $1.3\text{--}5.6 \times 10^4$, which increased with the monomer concentration. However, the molecular weight distribution (MWD) is widened with the monomer concentration. For example, when the monomer concentration is 0.05 mol/L, the MWD of PDDMA is about 1.34, but the MWD changed to 2.59 when the monomer concentration increased to 0.52 mol/L.

Effect of Polymerization Temperature, Time, and Concentration of Monomer and Initiator on Extent of Cyclization (f_c) of PDDMA

f_c could be determined by the bromination of the residual double bond, the variation of 1640 cm^{-1} , and the area at 5.3 and 6.3 ppm of >C=CH_2 in IR and NMR, respectively. The measurement results are shown in Tables I–III.

From Tables I–III, we observed that the f_c values obtained from the different measurement methods are very approximate to each other and all of them increase with increase of the polymerization temperature and prolonging of the reaction time and a decrease in the DDMA concentration.

The ratio of the intramolecular cyclization rate

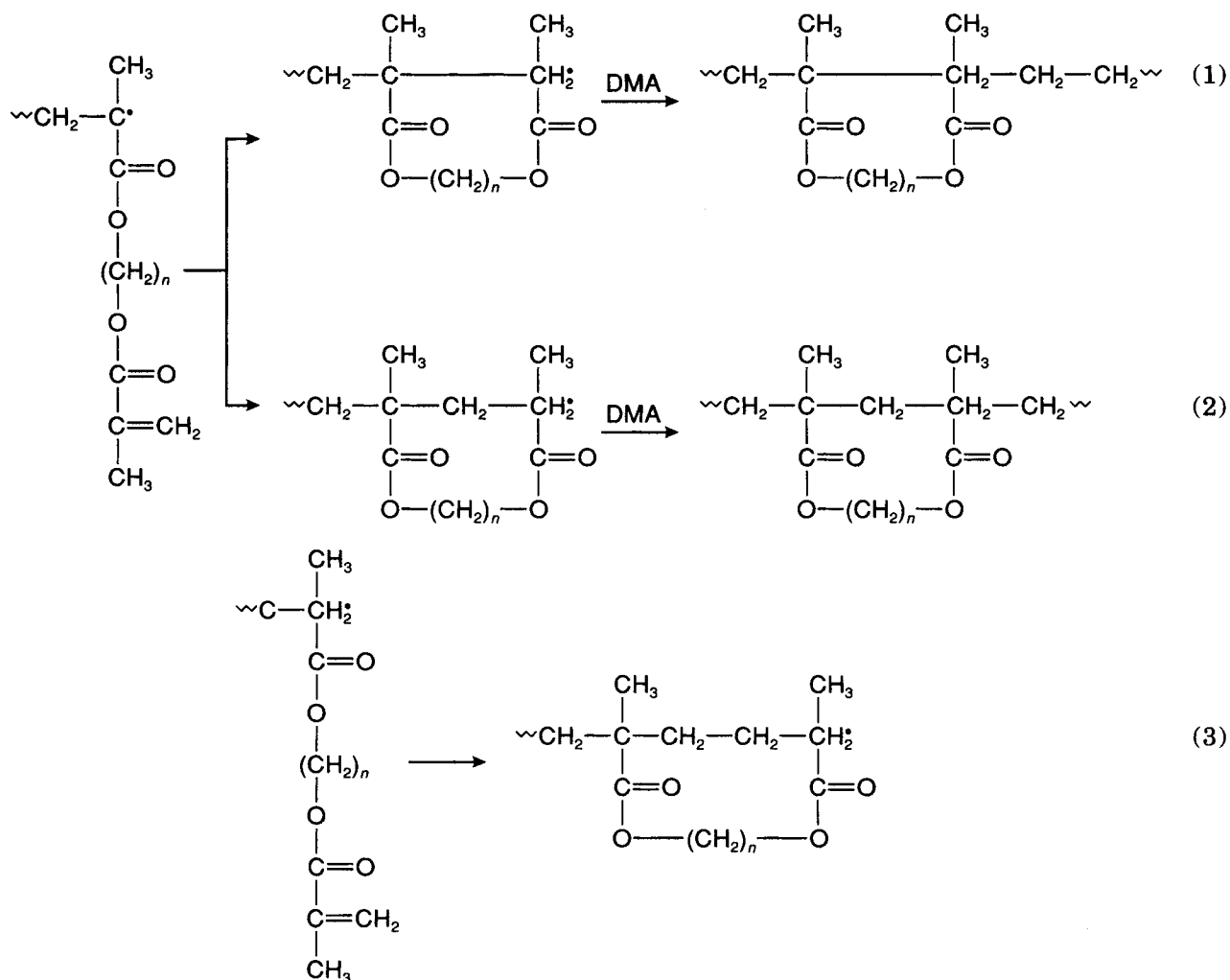
(R_c) and intermolecular propagation (R_p) could be derived from eq. (1):

$$\frac{1}{f_c} = \frac{R_c + R_p}{R_c} = 1 + \frac{2K_p[M]}{K_c} \quad (2)$$

The plots of $(1/f_c - 1)$ vs. $[M]$ according to eq. (2) are indicated in Figure 4, and the value of K_p/K_c are obtained from the slope of the straight line which did not pass the original point, i.e., when $[M]_0 = 0$, $1/f_c \neq 0$. This derivation may be caused by the approximation in which $[M]$, the concentration of the monomer at some specific time, was replaced by $[M]_0$, the starting concentration of monomer, in the condition of low conversion. If the Arrhenius expression was inserted into eq. (2), then the difference in activation energies ($E_c - E_p$) could also be obtained from the slope of the straight line in the plots of $1/f_c(1/f_c - 1)$ with the reciprocal of absolute temperatures at a constant monomer concentration ($[M] = 0.1$; Fig. 5); the value is 5.7 kJ/mol, i.e., the activation energy for intramolecular cyclization was 5.7 kJ/mol greater than the intermolecular propagation.

Structure Analysis of Cyclized PDDMA

As we well know, there are different types of addition modes for the attack of a growing chain radical of PDDMA on a monomer according to the cyclization mechanism:



The first step of route one is intramolecular ht addition and then intermolecular tt addition. For routes two and three, the first steps are intramolecular ht and intramolecular tt additions and then intermolecular ht and intermolecular hh additions, respectively.

To determine the contents of hh and ht additions in the polymer chain, PDDMA was hydrolyzed with concentrated sulfuric acid and methylated with diazomethane in diethyl ether; then its ^{13}C -NMR spectra was compared with the model compounds. The results are shown in Figure 6. There are no significant differences for either sample, i.e., the chemical shifts of PMMA derived from the hydrolyzed and methylated PDDMA are almost identical to those from the radical polymerization of MMA, which is in agreement with the chemical shifts calculated for the ht structure. The chemical shifts for both PMMA are summarized in Table IV.

Therefore, it could be concluded that intramolecular propagation in the cyclopolymerization of

DDMA is conformed mainly by the ht cyclization that leads to formation of a 20-membered ring in the polymer chain. There is no obvious effect of the increasing of the polymerization temperature (from 60 to 130°C) on the variation of ht and tt contents in the polymer chain, although many researchers reported that it is beneficial to form the formation of the tt structure in the higher polymerization temperature.¹⁶

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