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(40) In a paper which appeared after submission of our manuscript, Flory and co-workers (Erman, B.; Wagner, W.; Flory, P. J. *Macromolecules* **1980**, *13*, 1554) used the data of Oppermann and Rehage[13] and Mark and co-workers[10] to argue that the results of Valles and Macosko[12] were in error. Figures 5 and 6 show that when the number of elastically active strands are properly accounted for, the data of Mark's group are in good agreement with those of Valles and Macosko. These studies give significantly higher modulus values than those reported by Oppermann and Rehage for tetrafunctional networks. Experimental errors in making model networks always lead to a lower rather than a higher modulus, if one can exclude the presence of a second phase such as filler particles, precipitate, or stress-induced crystals. It is interesting to note that when the small-strain data of Flory and co-workers on poly(ethyl acrylate) networks are examined (not done in the paper), plots similar to our Figures 4–8 are obtained with a large nonzero intercept.

Radical-Initiated Homo- and Copolymerizations of Chloromethyl Methacrylate

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ABSTRACT: The kinetics of chloromethyl methacrylate (CMMA) homopolymerization has been investigated in benzene, using azobis(isobutyronitrile) as an initiator. The rate of polymerization (R_p) could be expressed by $R_p = k[\mathrm{AIBN}]^{0.5}[\mathrm{CMMA}]^{1.0}$. The overall activation energy was calculated to be 69.5 kJ/mol. Kinetic constants for CMMA polymerization were obtained as follows: $k_p/k_t^{1/2} = 0.14\ \mathrm{L}^{1/2}\cdot\mathrm{mol}^{-1/2}\cdot\mathrm{s}^{-1/2}$; $2fk_d = 9.4 \times 10^{-6}\ \mathrm{s}^{-1}$. The values of K and a in the Mark–Houwink equation, $[\eta] = KM^a$, were $K = 1.0 \times 10^{-4}$ and $a = 0.725$ when $M = \bar{M}_n$. The relative reactivity ratios of CMMA (M_2) copolymerizations with styrene ($r_1 = 0.21$, $r_2 = 0.31$) and methyl methacrylate ($r_1 = 0.47$, $r_2 = 1.03$) were obtained. Applying the Q–e scheme (in styrene copolymerizations) led to $Q = 1.25$ and $e = 0.85$. This value of e is higher than the value of e for β-chloroethyl methacrylate. Thermogravimetry of poly(CMMA) showed a 10% weight loss at 265 °C in air. The glass transition temperature (T_g) of poly(CMMA) was observed to be 75–80 °C by thermomechanical analysis.

Introduction

Many reports have been published on the correlation between the structure and the reactivity of vinyl monomers in their radical polymerizations and copolymerizations.[1-5] Otsu and co-workers[1] have studied the reactivity of alkyl methacrylates toward the styryl radical and found that their relative reactivities depend on the polar effects of the alkyl groups but not on steric factors. Therefore, the introduction of heteroatoms into the alkyl groups of alkyl methacrylates is expected to increase the polar effects, thereby modifying their reactivities in radical polymerization. However, no detailed study of the radical polymerization of such monomers has been carried out. Thus, we have initiated an investigation of the radical polymerization reactivities of methacrylic esters containing heteroatoms at the α position of alkyl groups. The first such monomer investigated is that containing the chloromethyl group at the α position. The present paper describes kinetic studies of the radical polymerization of CMMA and properties of the resulting polymer. In addition to these results, homo- and copolymers of CMMA are currently being studied for potential lithographic applications.

Experimental Section

Materials. Azobis(isobutyronitrile) (AIBN) was recrystallized from methanol. Benzene was successively washed with concentrated sulfuric acid, dilute sodium hydroxide, and distilled water, dried over calcium chloride, and distilled. The other reagents were used without further purification.

Monomers. Styrene (St) and methyl methacrylate (MMA) were purified by usual methods.

Preparation of Chloromethyl Methacrylate (CMMA). This monomer was prepared according to the procedure of Yakubovich et al.[6] To methacryloyl chloride (40 g, 0.38 mol) and paraformaldehyde (11.5 g, 0.38 mol) was added zinc chloride (1.2 g, 8.8×10^{-3} mol) (ice-bath cooling). After 15 min, the reaction mixture was stirred for 1 h at room temperature and then at 60–65 °C for 1 h. The filtrate was fractionated. After redistillation, 25–33 g (50–65%) of CMMA was obtained: bp 54–55 °C (21 mmHg) [lit.[6] bp 63–65 °C (62 mmHg)]; IR $\nu_{C=O}$ 1740, $\nu_{C=C}$ 1635, ν_{CH_2Cl} 1260 cm^{-1}; NMR (in $CDCl_3$) δ 6.1 (1 H, vinyl protons), 5.6 (1 H, vinyl protons), 5.65 (2 H, methylene protons), 1.95 (3 H, methyl protons); UV (95% ethanol) λ_{max} 208.2 nm (ϵ_{max} 4910).

Homopolymerization of Chloromethyl Methacrylate. Solution Polymerization. CMMA (0.97 g, 7.16 mmol), AIBN (1.8 mg, 1.1×10^{-2} mmol), and 10 mL of dry benzene were charged to a polymerization tube and then degassed (three freeze–thaw–pump cycles). The tube was sealed and heated at 60 °C for 48 h and then opened, and the solution was diluted with benzene. The polymer was precipitated into excess methanol with vigorous stirring. A white fibrous polymer was obtained in >95% yields, exhibiting $[\eta] = 0.57$ dL/g in tetrahydrofuran at 30 °C.

Emulsion Polymerization. Into a 250-mL three-necked flask, fitted with a condenser, a thermometer, a nitrogen inlet, and a magnetic stirrer, were placed 30 mL of distilled degassed water, sodium lauryl sulfate (0.2 g, 6.9×10^{-4} mol), and $K_2S_2O_8$ (0.02 g, 7.4×10^{-5} mol). Nitrogen was passed through the solution for 15 min. Then CMMA (10 g, 0.096 mol) was added and the reaction mixture was heated at 50 °C with vigorous magnetic stirring. After 24 h, the resulting polymer latex was coagulated into 300 mL of methanol. The precipitate was filtered and dried in vacuo overnight at 40 °C to give 8.7 g (87%) of polymer: $[\eta]$

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Table I
Relationship between R_p and Initiator Concentration[a]

[AIBN] × 10^3, mol/L	polymerization time, min	yield, %	R_p × 10^5, mol/(L·s)	[η],[b] dL/g	$\overline{M}_n$ × 10^{-5} [c]	R_p/[AIBN]$^{1/2}$
0.304	177	7.75	0.946	1.26	4.5	1.71
0.730	105	6.43	1.32	0.92	3.0	1.54
1.82	60	6.23	2.24	0.70	1.8	1.66
4.87	35	6.10	3.77	0.44	1.1	1.71

[a] [CMMA] = 1.30 mol/L, solvent = benzene, temperature = 60 °C. [b] At 30 °C in tetrahydrofuran. [c] Measured by membrane osmometry at 25 °C in tetrahydrofuran.

= 1.9 dL/g (tetrahydrofuran, 30 °C); IR $\nu_{C=O}$ 1750, ν_{CH_2Cl} 1250 cm^{-1}. Anal. Calcd: C, 44.63; H, 5.24. Found: C, 44.83; H, 5.6.

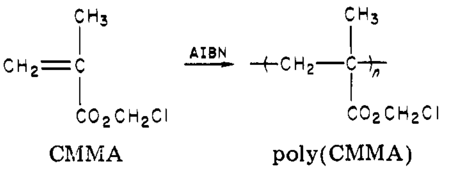
Conversion of Poly(chloromethyl methacrylate) to Poly(methyl methacrylate). Poly(chloromethyl methacrylate) was hydrolyzed with concentrated sulfuric acid at room temperature for 2 days. The solution was poured into water and the precipitated polymer was collected. The polymer was redissolved in aqueous alkaline solution and reprecipitated from an acidic solution. The resulting poly(methacrylic acid) was converted to poly(MMA) with diazomethane in benzene and then precipitated from methanol. The triad tacticity of poly(MMA) was determined by the intensity of the α-methyl signal in the ^{1}H NMR (90 MHz) spectra measured in $CDCl_3$ at 35 °C.

Kinetics. Weighed amounts of monomer, solvent, and initiator were charged into tubes, followed by degassing at 5 × 10^{-3} torr by three alternate freeze–thaw cycles. After the tubes were sealed, they were placed in a constant-temperature bath for specified times. After removal from the bath, the polymer was precipitated into excess methanol, filtered, dried in vacuo at 40 °C for 48 h, and weighed. The composition of the copolymers was calculated from elemental analyses.

Measurements. The infrared spectra were recorded on a JASCO IRA-1 spectrophotometer, the ultraviolet spectra on a Hitachi Model 100-60 spectrophotometer, and the NMR spectra on either a Hitachi R-24B (60 MHz) or a Hitachi R-22 (90 MHz) instrument. The glass transition temperature was measured on a Shimadzu TMA-30 instrument at a heating rate 20 °C/min in air. The thermogravimetry was performed with a Shimadzu TG-20B thermal balance. The temperature range investigated was from room temperature to 600 °C. Membrane osmometry (MOSM) was performed with a Hewlett-Packard Model 501 osmometer at 25 °C in tetrahydrofuran. Viscosity measurements were made with a Ubbelohde viscometer at 30 °C in tetrahydrofuran.

Results and Discussion

Homopolymerization of Chloromethyl Methacrylate. Homopolymerizations were readily conducted in both solution and emulsion systems. Solution polymerization was conducted at 60 °C, but emulsion polymerization was carried out at 50 °C to avoid hydrolysis of the ester, which becomes serious at temperatures greater than 65 °C.



$$CH_2{=}C(CH_3)(CO_2CH_2Cl) \xrightarrow{AIBN} -\!\!\left(CH_2-C(CH_3)(CO_2CH_2Cl)\right)\!\!-_n$$

CMMA poly(CMMA)

The homopolymer is a white solid. Films can be cast from chloroform. The homopolymer is very soluble in common solvents, such as tetrahydrofuran, acetone, benzene, and acetonitrile, and it is insoluble in methanol.

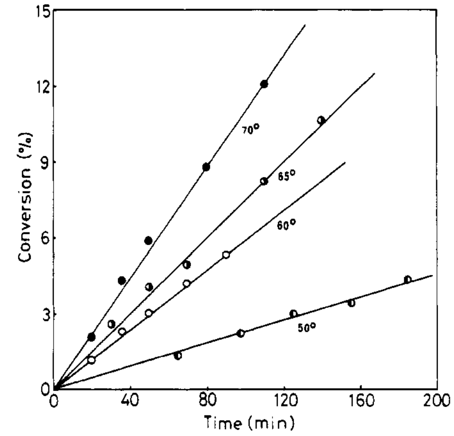


Figure 1. Time–conversion curves for solution polymerization of CMMA in benzene at (◐) 50, (○) 60, (◑) 65, and (●) 70 °C. [CMMA] = 0.753 mol/L, [AIBN] = 8.30 × 10^{-4} mol/L.

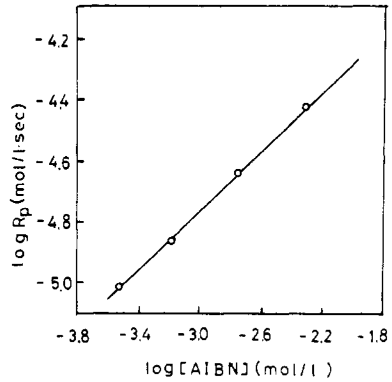


Figure 2. Plots of log R_p against log [AIBN] for homopolymerization of 1.30 mol/L CMMA in benzene at 60 °C.

Table II
Relationship between R_p and Monomer Concentration[a]

[CMMA], mol/L	polymerization time, min	yield, %	R_p × 10^5, mol/(L·s)	R_p/[CMMA]
0.607	150	17.2	1.16	1.91
0.877	150	17.4	1.70	1.94
1.13	150	17.7	2.22	1.96
1.36	120	14.7	2.79	2.05

[a] [AIBN] = 3.65 × 10^{-3} mol/L, solvent = benzene, temperature = 60 °C.

Kinetic Study. The solution homopolymerization of CMMA in benzene was initiated with AIBN at temperatures from 50 to 70 °C. The time–conversion curves, shown in Figure 1, were linear and without an induction period. Table I shows the relationship between R_p and initiator concentration at 60 °C. A plot of log R_p against log [AIBN], shown in Figure 2, is a straight line with a slope of 0.5. Table II summarizes the relationship between R_p and monomer concentration in polymerizations at 60 °C. A plot of log R_p vs. log [CMMA] (Figure 3) has a slope of 1.0. The rate equation for the homopolymerization of CMMA in benzene may be given, therefore, as

$$R_p = k[AIBN]^{0.5}[CMMA]^{1.0} \qquad (1)$$

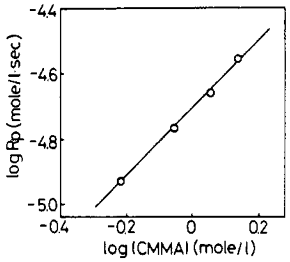


Figure 3. Plots of log R_p against log [CMMA] for homopolymerization of CMMA in benzene at 60 °C. [AIBN] = 3.65 × 10^{-3} mol/L.

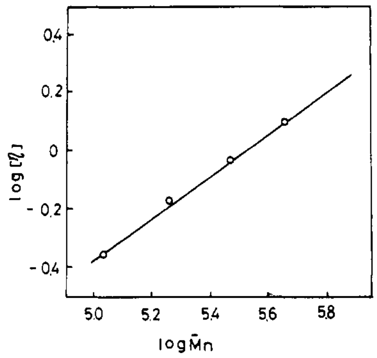


Figure 4. Plots of log [η] against log $\bar{M}_n$. Solvent = THF, temperature = 25 °C.

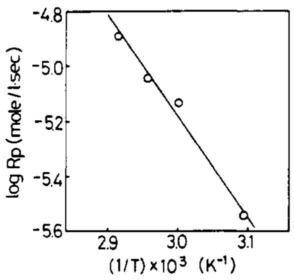


Figure 5. Arrhenius plot of log R_p against $1/T$ for polymerization of CMMA.

where k is an overall rate constant.

Number-average molecular weights ($\bar{M}_n$) were measured at 25 °C in tetrahydrofuran by membrane osmometry. A double-logarithmic plot of intrinsic viscosity vs. molecular weight is shown in Figure 4. Plots were linear and correspond to

$$[\eta] = 10^{-4} \times \bar{M}_n^{0.725} \qquad (2)$$

An Arrhenius plot (Figure 5) showed the overall activation energy, E_a, to be 69.5 kJ/mol. In the presence of an initiator, the overall activation energy for the normal kinetic scheme is given by

$$E_a = E_d/2 + E_p - E_t/2 \qquad (3)$$

where E_d, E_p, and E_t are the activation energies for the initiation, propagation, and termination steps, respectively. Using the literature value of 128 kJ/mol[7] for E_d, one can calculate a value of 5.5 kJ/mol for $E_p - E_t/2$ for CMMA in benzene. This may be compared with the literature value of 20.5 kJ/mol[8] for $E_p - E_t/2$ for MMA.

For polymerizations following the normal kinetic scheme, the relation between the number-average degree of polymerization, $\bar{P}_n$, and R_p is given by [9]

$$1/\bar{P}_n = C_M + C_I[I]/[M] + C_S[S]/[M] + AR_p/[M]^2 \qquad (4)$$

where C_M, C_I, and C_S are the chain transfer constants to monomer, initiator, and solvent, respectively. [M] and [S] are the concentrations of monomer and solvent. When AIBN is used as an initiator, $C_I = 0$ and eq 4 reduces to

$$1/\bar{P}_n = C_M + C_S[S]/[M] + A'R_p \qquad (5)$$

where A' and R_p are defined by eq 6 and 7, respectively.

$$A' = k_t/k_p^2[M]^2 \qquad (6)$$

$$R_p = (2fk_d)^{1/2}(k_p/k_t^{1/2})[I]^{1/2}[M] \qquad (7)$$

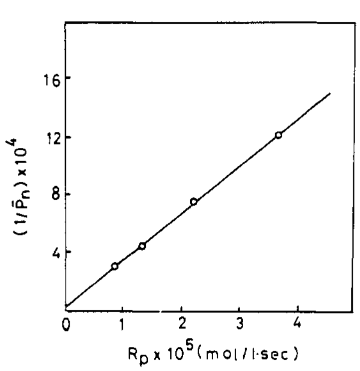


Figure 6. Plots of $1/\bar{P}_n$ against R_p. [CMMA] = 1.30 mol/L, [AIBN] = (0.304–4.87) × 10^{-3} mol/L, solvent = benzene, temperature = 60 °C.

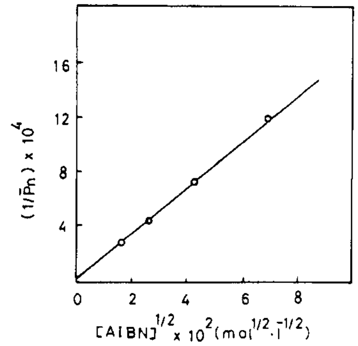


Figure 7. Plots of $1/\bar{P}_n$ against $[AIBN]^{1/2}$. [CMMA] = 1.30 mol/L, [AIBN] = (0.304–4.87) × 10^{-3} mol/L, solvent = benzene, temperature = 60 °C.

A plot of the reciprocal of the $\bar{P}_n$ against R_p from Table I is shown in Figure 6. From its slope, k_t/k_p^2 was estimated to be 54 mol·s·L^{-1}. C_M and C_S are too small to measure accurately. A plot of $1/\bar{P}_n$ against [AIBN], shown in Figure 7, was linear, and from its slope $(2fk_dk_t)^{1/2}/k_p$ was estimated to be 2.25 × 10^{-2} $mol^{1/2}{\cdot}L^{-1/2}$. From these values, $k_p/k_t^{1/2}$ and $2fk_d$ were calculated to be 1.4 × 10^{-1} $L^{1/2}{\cdot}mol^{-1/2}{\cdot}s^{-1/2}$ and 9.4 × 10^{-6} s^{-1}, respectively. Using the reported rate constant for AIBN decomposition[10] (k_d = 8.45 × 10^{-6} s^{-1} at 60 °C in benzene) yields a calculated initiator efficiency of 0.56. Values of $k_p/k_t^{1/2}$ for MMA of 0.087[11] and 0.085[8] have been determined. Thus, $k_p/k_t^{1/2}$ for CMMA was about 1.6 times larger than that for MMA.[8,11]

Copolymerizations. The copolymerizations of CMMA with styrene and methyl methacrylate were carried out in benzene at 60 °C. The results are given in Table III. The copolymer composition was determined by elemental analysis. The monomer–copolymer composition curves are shown in Figure 8. The values of r_1 and r_2 were obtained by a nonlinear least-squares computer fit of the integrated form of the copolymer equation described previously.[12] Q–e values for CMMA, calculated from monomer reactivity ratios, are listed in Table IV, where the values for β-chloroethyl methacrylate and ethyl methacrylate are shown

Table III
Copolymerization of CMMA with Styrene and Methyl Methacrylate^a

[monomer], mol %		polymerization time	copolymer yield, %	CMMA content, mol %
M_1	M_2			
St	CMMA			
0.948	0.052	3 h 30 min	5.2	0.177
0.813	0.187	7 h	12.8	0.342
0.762	0.238	2 h 30 min	9.0	0.392
0.652	0.348	6 h 30 min	18.7	0.446
0.552	0.448	6 h	20.0	0.492
0.450	0.550	2 h	9.1	0.530
0.379	0.621	6 h	24.0	0.568
0.365	0.635	1 h 40 min	7.6	0.581
0.250	0.750	1 h 30 min	8.4	0.642
0.130	0.870	1 h 30 min	9.2	0.767
MMA	CMMA			
0.920	0.080	40 min	6.4	0.141
0.841	0.159	40 min	6.3	0.229
0.767	0.233	30 min	4.8	0.340
0.674	0.326	30 min	4.8	0.427
0.580	0.420	30 min	4.8	0.553
0.480	0.520	30 min	4.6	0.580
0.376	0.624	25 min	3.6	0.681
0.269	0.731	25 min	3.9	0.741
0.140	0.860	20 min	3.8	0.875

^{a} [AIBN] = 5.08×10^{-3} mol/L. Solvent = benzene, temperature = 60 °C.

Table IV
Copolymerization Parameters^a

M_1	M_2	r_1	r_2	r_1r_2	Q_2	e_2
St	CMMA	0.20	0.23	0.046	1.21	0.95
MMA	CMMA	0.50	1.03	0.515	2.06	1.22
St^b	CEMA^c	0.33	0.46	0.15	1.01	0.57
St^b	EMA^d	0.53	0.41	0.22	0.70	0.44

^{a} St: $Q_1 = 1.00$, $e_1 = -0.80$; MMA: $Q_1 = 0.74$, $e_1 = 0.40$. ^{b} From ref 13. ^{c} CEMA = β-chloroethyl methacrylate. ^{d} EMA = ethyl methacrylate.

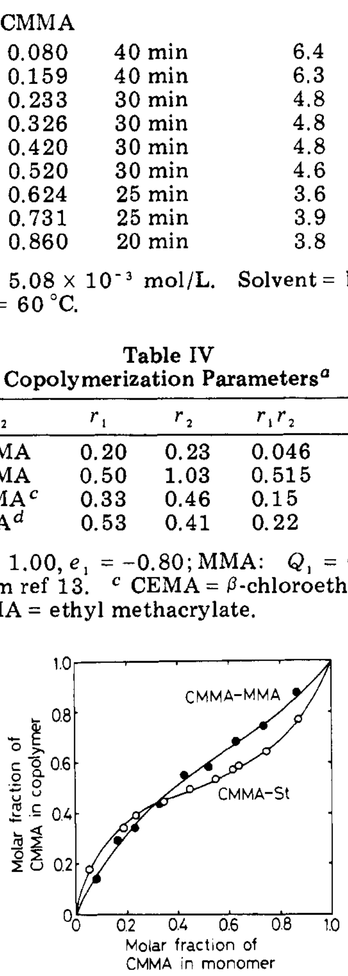


Figure 8. Copolymerizations of CMMA with St (○) and MMA (●).

for comparison.[13] The electron withdrawing inductive effect of the chloromethyl group is clearly manifest in the e values for CMMA (0.95) vs. that for methyl methacrylate (0.40). Table IV illustrates the significantly higher general reactivity of CMMA over MMA and the higher tendency of CMMA to alternate with styrene. It also points out that the Q–e scheme is only a semiquantitative approximation.

It has been shown that the reactivities of alkyl methacrylates toward the styrene radical correlate quite well with the Taft σ^* constants of alkyl groups;[1] that is

$$\log (1/r_1) = \rho\sigma^* + \text{constant} \qquad (8)$$

The σ^* constants of the chloromethyl and chloroethyl groups are 1.05 and 0.38. Thus, the larger positive e value of CMMA vs. methyl methacrylate and chloroethyl methacrylate is easily understood. Employing $r_1 = 0.21$ (from styrene/CMMA copolymerizations) and $\sigma^*(CH_2Cl) = 1.05$, eq 8 was used to calculate $\rho = 0.35$. This value was consistent with the reported value of 0.33.[1] It is also of interest that the introduction of a chlorine atom into the methyl group effectively decreased the E_p and increased the rate of polymerization.

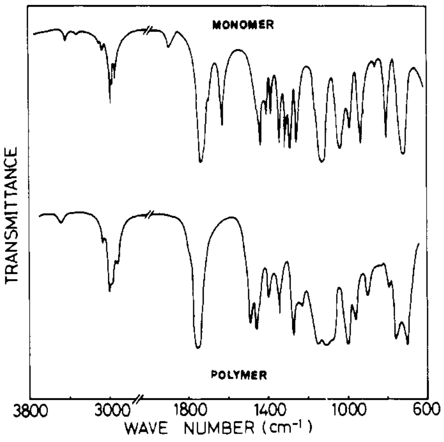


Figure 9. Infrared spectra of CMMA and poly(CMMA).

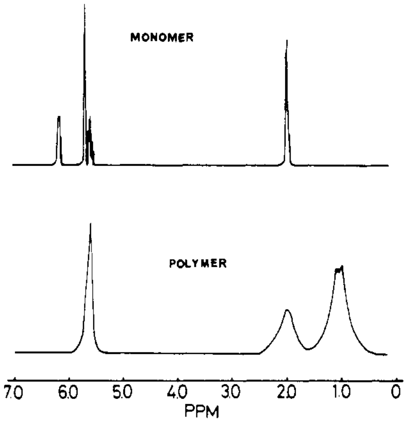


Figure 10. NMR spectra of CMMA and poly(CMMA) in $CDCl_3$ with internal Me_4Si reference.

Polymer Characterization. The homopolymer gave a satisfactory elemental analysis. The IR spectra of CMMA and poly(CMMA) are shown in Figure 9. The C=O bond stretching at 1740 cm^{-1} and the C=C bond stretching at 1635 cm^{-1} are clearly observed for the monomer, whereas poly(CMMA) exhibited the C=O absorption at 1750 cm^{-1} and no trace of the C=C stretching was detected. The high frequency of the ester carbonyl group, due to the polar effect of chlorine, indicates that this ester is much more susceptible to nucleophilic attack than a normal ester.

The NMR spectra of CMMA (Figure 10) consisted of a multiplet for the methyl protons [δ 1.95 (3 H)], two multiplets for the vinyl protons [δ 5.6 (1 H), 6.1 (1 H)], and a singlet for the methylene protons [δ 5.65 (2 H)]. The NMR spectra of poly(CMMA) exhibited a singlet at δ 5.5 (2 H), a broad peak at δ 1.9 (2 H), and a multiplet at δ 1.0 (3 H), which are assigned to the CH_2Cl protons, β-methylene protons, and α-methyl protons, respectively. To obtain information on tacticity, poly(CMMA) was converted to poly(MMA) by hydrolysis in sulfuric acid at 20–25 °C, followed by methylation with diazomethane. The tacticity of poly(MMA) determined by ^1H NMR was 8% isotactic, 46% heterotactic, and 46% syndiotactic.

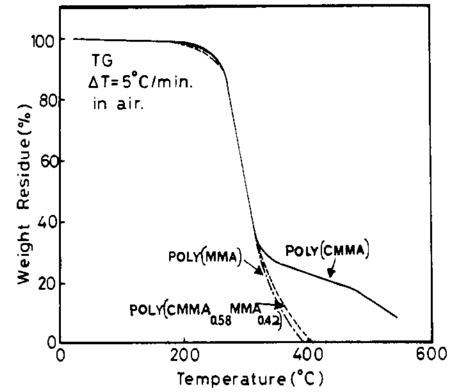


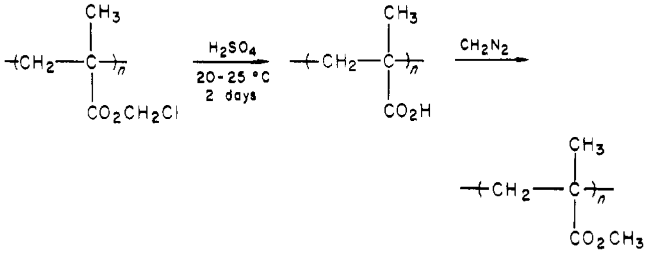
Figure 11. TG curves of poly(CMMA), poly(CMMA–MMA), and poly(MMA).

Table V
Thermal Characterization of Polymers

polymer	mole ratio $[M_1]/[M_2]$ in copolymer	degradation temp,[a] °C init wt loss in air	10% wt loss in air
poly(MMA) (M_1)		240	260
poly(CMMA) (M_2)		210	265
poly(MMA-CMMA)	77/23	200	275
poly(MMA-CMMA)	57/43	195	250
poly(MMA-CMMA)	42/58	180	265
poly(MMA-CMMA)	26/74	170	270

[a] Observed by TGA at a heating rate of 5 °C min^{-1}.

Thus, CMMA, like most other methacrylates, gave a syndiotactic polymer with radical initiators.



The glass transition temperature (T_g) of poly(CMMA) was observed at 75–80 °C by thermomechanical analysis (TMA). This may be compared to the reported T_g value of about 105 °C[14] for poly(MMA). No melting point was observed for poly(CMMA), in agreement with its X-ray diffraction pattern, which showed very little crystalline structure. Thermogravimetry (TG) was carried out in air at a heating rate of 5 °C/min on poly(CMMA) and on a 58:42 CMMA/MMA copolymer. Typical thermograms are shown in Figure 11, where a thermogram for poly(MMA) is included for comparison. The degradation temperature for a 10% weight loss was 265 °C for poly(CMMA). This is comparable to that of poly(MMA). However, a small amount of residue remained up to 550 °C after rapid degradation. This may be compared to the TG curve of poly(MMA), where no residue remained. In poly(CMMA–MMA) copolymers, the initial degradation temperature decreased with increasing CMMA content, but such trends were not observed in the degradation temperature for 10% weight loss of the copolymers. These results are summarized in Table V.

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Binding of Zinc Ions to Polymethacrylate Anions at Varying Charge Densities

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ABSTRACT: The interaction of zinc ions with partly neutralized poly(methacrylic acid) (PMA) has been studied by using conductance, potentiometric titration, and equilibrium dialysis techniques. Partially neutralized PMA was titrated with a solution of zinc nitrate so as to enable the polymer/zinc ion ratio to be varied over a wide range. The results from potentiometric and conductance titrations show the existence of two types of complexes, one existing at low concentration and the other at high concentration of metal ions. Results from dialysis studies confirm the above observations and reveal that only one type of complex is stable. Equations were developed to enable calculations of the binding constants.

Introduction

Considerable importance and interest exist in the study of binding of counterions to polycarboxylates. The interaction between di- and trivalent cations with polyelectrolytes has been widely regarded as chelation of cations by neighboring[1-3] or widely separated[4,5] anionic groups. Various techniques have been used. Of the cations studied so far, copper[3,6,7] and cobalt[8] have received the greatest

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