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Spontaneous Polymerization of Methyl Methacrylate. 8. Polymerization Kinetics of Acrylates Containing Chlorine Atoms[†,‡]

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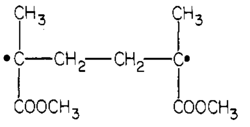
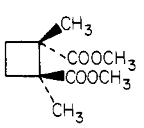
ABSTRACT: Chlorine-containing acrylate monomers polymerize spontaneously at much higher polymerization rates than methyl methacrylate. The results are interpreted in terms of an intramolecular catalysis of the intersystem crossing reaction of the intermediate biradical by the chlorine atom.

In the preceding parts of this series it was shown what effort has to be done to obtain reproducible kinetic results for the spontaneous polymerization of methyl methacrylate (MMA),[1] what oligomers are formed in side reactions,[2,3] and how they participate in the reaction sequence.[4,5] By the addition of strong transfer agents it became possible to trap biradical $\cdot M_2\cdot$[6] which was already thought to be responsible for initiation from activation parameters and the structure of cyclobutane-type dimers. At the same time, addition of transfer agents leads to a reasonable acceleration of the polymerization. This was attributed to a rising probability for the changeover from biradicals—with a high self-termination probability—to propagating monoradicals. The investigation of the spontaneous polymerization of MMA in halogen-containing "heavy-atom" solvents like CCl_4 or *n*-butyl bromide[7] revealed that besides the above transfer initiation, the multiplicity of biradical $\cdot M_2\cdot$ seems to be of importance: like a molecule in an excited-state biradical, $\cdot M_2\cdot$ may exist in a singlet and a triplet form, the first of which is expected to be formed thermally from two monomer molecules. Once the triplet state is reached by spin inversion (a reaction catalyzed by "heavy atoms" due to higher L–S coupling), self-termination is suppressed; i.e., self-termination is not possible before the biradical has returned to its singlet state. Experiments under inert gas atmosphere confirmed this interpretation: as in heavy-atom-containing solvents, inert gas xenon yields much higher rates of the spontaneous polymerization than values obtained in vacuo, while under nitrogen atmosphere no difference from the vacuum values could be detected within experimental error.



$\cdot M_2\cdot$



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In spectroscopy, where heavy-atom effects are quite familiar, a distinction is made between "external" and "internal" heavy atom effects. Table I[8] gives an example of triplet lifetimes for naphthalene in matrices containing halogen atoms and for the respective halonaphthalenes. The effect of "internal" heavy atoms, chemically bound to the spectroscopically investigated group, is much more pronounced. Consequently, it seemed to be of interest to analyze whether the integration of halogen atoms into acrylate monomers really leads to a much faster spontaneous polymerization as compared with MMA and by this to give further evidence for the mechanism including singlet and triplet biradicals $\cdot{}^1M_2\cdot$ and $\cdot{}^3M_2\cdot$. As model compounds, methyl α-chloroacrylate (MCA) and β-chloroethyl methacrylate (CEMA) were chosen. To exclude steric effects in CEMA, control experiments using ethyl methacrylate (EMA) were also included.

Table I

Effect of Internal and External Heavy Atoms on the Relative Rate of $T_1 \leftarrow S_1$ Intersystem Crossing (k_{isc}) and on the Relative Rate of Phosphorescence (k_{ph})[a]

1-X-substituted naphthalenes			naphthalene in MeOH/EtOH and *n*-PrX		
X	$k_{ph,rel}$	$k_{isc,rel}$	*n*-PrX	$k_{ph,rel}$	$k_{isc,rel}$
H	1	1		1	1
F	1.6	2			
Cl	8.6	150	*n*-PrCl	1.6	2
Br	250	5000	*n*-PrBr	4.0	25
I	2500	30000	*n*-PrI	6.8	140

[a] Data of ref 8.

Experimental Part

Methyl methacrylate (MMA) and β-chloroethyl methacrylate (CEMA) (unstabilized) were supplied by Röhm, Darmstadt. They were further treated as described in ref 1.

Ethyl methacrylate (EMA) (Merck) was destabilized by treatment with NaOH, dried over $CaSO_4$, and treated as above.

Methyl α-chloroacrylate (MCA) was synthesized starting from methyl acrylate (Röhm): First, by chlorination, methyl 2,3-dichloropropanoate was obtained[9] (bp 74 °C; NMR: CH_3O, 3.82 ppm (s); CHCl, 4.46 ppm (t), CH_2Cl, 3.43 ppm (d)), which on distillation with quinoline directly yields the monomer.[10] Due to the high reactivity, MCA had to be stabilized by 100 ppm of hydroquinone monomethyl ether. (Special care should be applied when handling MCA, since its vapors are strongly cauterizing. The monomer tends to polymerize "spontaneously" in the distillation column even at moderate temperatures. For this reason, experiments with the even more reactive methyl α-bromoacrylate were omitted).

Azobis(isobutyronitrile) (AIBN) (Merck) was recrystallized twice from ethanol (fp 92 °C). Azobis(cyclohexane-1-nitrile) (ACN) was synthesized from cyclohexanone, KCN, and hydrazinium sulfate[11] (fp 112.5 °C).

Kinetic experiments using initiator were followed dilatometrically. Dilatometers having 0.5-mL capillaries and reaction tubes of 10-mm diameter were calibrated twice with distilled, degassed water. Solutions of initiator in acetone were added and the solvent was carefully removed at about 50 mmHg. After addition of the respective monomer, oxygen was removed by three freezing–thawing cycles, applying vacuum of about 0.001 mmHg.

The spontaneous polymerization of the monomers was investigated gravimetrically as described for MMA;[1] i.e., the kinetic experiments were performed in sealed ampules, thoroughly excluding oxygen (by degassing and sealing under high vacuum), surface effects (by treatment of the inner surfaces of the ampules with dimethyldichlorosilane), and light (by using brown glassware).

[†] Dedicated to Professor Walter H. Stockmayer on the occasion of his 70th birthday with very best wishes.

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Table II
Kinetics of the AIBN-Initiated Polymerization of β-Chloroethyl Methacrylate

temp, °C	$[I_0] \times 10^3$	$[M_0]$	$R_p \times 10^5$	$[I_0]^{1/2} \times 100$	$k_{d,AIBN}$
40	8.01	7.30	6.89	8.95	3.78×10^{-7}
	1.77		3.38	4.21	
	4.90		5.54	7.00	
45	4.10	7.26	7.91	6.40	8.50×10^{-7}
	1.99		5.46	4.46	
	7.96		10.22	8.92	
50	6.29	7.22	15.44	7.93	1.86×10^{-6}
	2.60		10.23	5.10	
55	6.18	7.19	25.08	7.86	3.98×10^{-6}
	3.54		18.28	5.95	
	1.32		11.79	3.64	
60	0.78	7.15	13.98	2.79	8.31×10^{-6}
	0.38		10.15	1.95	
	2.18		23.59	4.67	
	2.84		27.21	5.33	
	1.48		19.15	3.85	

Table III
Kinetics of the ACN-Initiated Polymerization of Methyl α-Chloroacrylate

temp, °C	$[I_0] \times 10^3$	$[M_0]$	$R_p \times 10^5$	$[I_0]^{1/2} \times 100$	$k_{d,ACN}$
70	0.193	9.56	3.95	1.39	1.88×10^{-6}
	0.458		7.39	2.14	
	0.552		8.18	2.35	
80	0.149	9.46	10.36	1.22	6.26×10^{-6}
	0.303		14.70	1.74	
	0.480		20.38	2.19	
90	0.046	9.36	15.20	0.68	1.95×10^{-5}
	0.088		21.05	0.94	
	0.174		29.20	1.32	
	0.306		39.17	1.75	

The polymerization reactions were carried out at the given temperature ±0.1 °C. After conversions of about 5% were reached, the reaction vessels were cooled and broken, the reaction mixture was diluted with acetone, chloroform, or DMF, and the polymer was precipitated in methanol or petroleum ether (40/80). The polymers were dried in vacuo at 50 °C.

Densities were determined according to Kratky, Leopold, and Stabinger[12] in a Heraeus U-tube densitometer DMA 50. The values obtained for the specific volumes of the monomers and the apparent specific volumes of the polymers (<5% in degassed monomer) were as follows: EMA, $v_{sp} = 1.0674 + 1.380 \times 10^{-3}T$ (°C); CEMA, $v_{sp} = 0.8835 + 0.959 \times 10^{-3}T$ (°C); MCA (stabilized with 100 ppm of hydroquinone), $v_{sp} = 0.8146 + 0.961 \times 10^{-3}T$ (°C); PEMA, $v_{sp} = 0.8621 + 0.516 \times 10^{-3}T$ (°C); PCEMA, $v_{sp} = 0.7366 + 0.317 \times 10^{-3}T$ (°C); PMCA (in stabilized monomer), $v_{sp} = 0.6129 + 0.480 \times 10^{-3}T$ (°C).

Molecular weight determinations were carried out on a Hewlett-Packard GPC having Polymer Laboratories Styragel columns. Light scattering results were obtained with a Fica 50 instrument. The $\partial n/\partial c$ values necessary for the evaluation were determined according to Bodmann[13] (436 nm): PCEMA in toluene, $(\partial n/\partial c)_{25 °C} = 2.04 \times 10^{-2}$ L/g; PCEMA in acetone, $(\partial n/\partial c)_{25 °C} = 13.87 \times 10^{-2}$ L/g; PCEMA in THF, $(\partial n/\partial c)_{25 °C} = 9.87 \times 10^{-2}$ L/g; PMCA in DMF, $(\partial n/\partial c)_{25 °C} = 6.28 \times 10^{-2}$ L/g.

Viscosity measurements were carried out in automated Ubbelohde viscometers, using toluene (PMMA, $[\eta] = 7.1 \times 10^{-3}\bar{M}_\eta^{0.73}$ [14]), methyl ethyl ketone (PEMA, $[\eta] = 2.83 \times 10^{-3}\bar{M}_\eta^{0.79}$ (23 °C)[15]), acetone, THF (PCEMA), and DMF (PMCA) solvents at 25 °C.

A detailed analysis of the oligomers (cf. MMA[3]) was not included, since the oligomers of most interest, having the cyclobutane structure, were not expected to be formed at a faster rate than those of MMA. Taking into account the much faster rate of polymerization of CEMA and MCA, the cyclobutane dimers are formed in amounts below accessibility by GC.

Kinetics of the Initiated Polymerization of MCA and CEMA

For both monomers, only very few kinetic data are available in the literature, which do not permit extrapolation to temperatures necessary to investigate the spontaneous polymerization. Therefore polymerizations initiated by AIBN (CEMA, 40–60 °C) and ACN (MCA, 70–90 °C) were carried out to obtain the values for k_p^2/k_t necessary for further calculations. The results of these experiments are given in Tables II and III. Yokota et al.[16] determined the initiating efficiencies f for a series of monomers by scavenging the primary radicals with DPPH. For the evaluation of the k_p^2/k_t of CEMA, their value $f = 0.58$ was used, while for MCA, f was arbitrarily set to 0.5, which results in a possible error of about 20% in k_p^2/k_t. Values of k_p^2/k_t for EMA were mainly taken from the literature;[16–19] two values determined in our laboratory, using $f = 0.74$,[16] are also included in Figure 1. From the Arrhenius plot the following equations result: EMA, $\ln k_p^2/k_t = 7.92 - 4263/T$; CEMA, $\ln k_p^2/k_t = 10.42 - 4462/T$; MCA, $\ln k_p^2/k_t = 14.77 - 5808/T$.

Spontaneous Polymerization of EMA, CEMA, and MCA

The results of the kinetics of the spontaneous polymerization of the above monomers are given in Table IV and Figure 2. For the evaluation the validity of the biradical mechanism was assumed, i.e., a dependence of the overall rate of polymerization on the square of the monomer concentration. The results of the "external" heavy-atom effect[7] indicate that the external effect by surrounding monomer molecules "as solvent" may not be excluded. Table I shows, however, that this should yield only a rather small term of 2.5th order in monomer for R_p.

Figure 2 and Table V show the Arrhenius plot for the initiation constant and the resulting activation parameters, respectively. While steric effects do not play an important role, at least for the ethyl substituent, the substitution by a chlorine atom leads to much higher rate constants of initiation.

For the interpretation, two effects must be considered:

1. Differences in the activation energy may be related to differences in the energies of biradical formation.

Table IV
Kinetics of the Spontaneous Polymerization of EMA, CEMA, and MCA[a]

monomer	temp, °C	$R_{p,0} \times 10^7$	$[M_0]$	$k_p^2/k_t \times 100$	$k_i \times 10^{16}$
EMA	120	1.58	7.11	5.38	1.81
	140	7.06	6.96	9.09	23.4
CEMA	100	3.00	6.87	21.5	1.88
	110	6.51	6.81	29.4	6.70
	120	13.3	6.74	39.5	21.70
	140	58.4	6.62	68.4	259.6
MCA	80	13.4	9.31	18.7	12.8
	90	34.0	9.21	29.4	54.6
	100	68.3	9.11	45.2	149.8
	110	181.2	9.01	67.8	734.8
MMA[7]	130	4.95	8.13	9.17	6.1
	130	5.20	8.13	9.17	6.8
	130	7.43	8.13	9.17	13.7
MMA/CCl$_4$	130	35.4	3.72	11.98	
MMA/*n*-BuCl	130	0.79	2.02	8.25	

[a] k_i was calculated by assuming the applicability of the mechanism derived for MMA. Values of MMA are given for comparison. k_i cannot be given for the external heavy-atom effect due to different reaction orders (cf. ref 7).

Table V
Activation Parameters of the Initiation Constant of the Spontaneous Polymerization

monomer	ln *A*	E_a, kJ/mol	time to 5% conv at 120 °C, h
MMA EMA	7.3	138.3	380
CEMA	14.5	158	47
MCA	16.0	148	<1

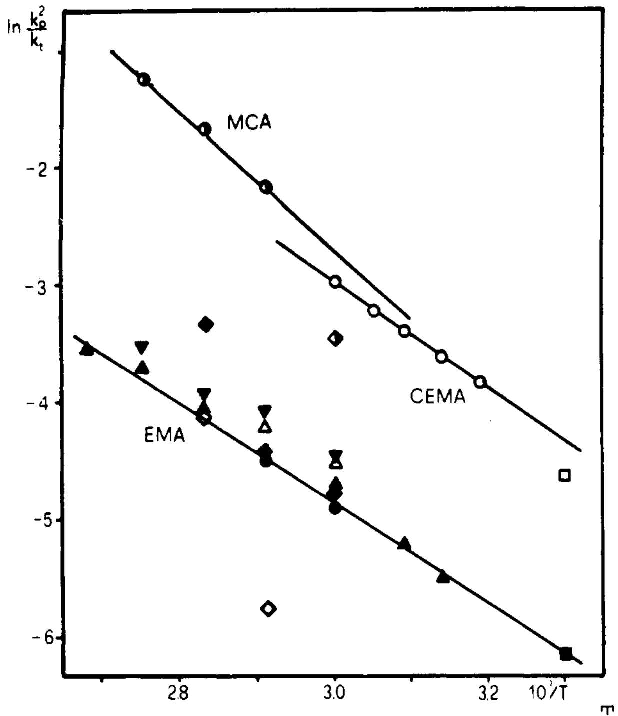

Figure 1. Arrhenius plot of k_p^2/k_t: (●, ■, ▲, ▼, ◈) EMA; (△, ○, □, ◇) CEMA; (◐, ◈) MCA; (●, ○, ◐) this work; (■, □) ref 16; (▲) ref 17; (◈) ref 22; (▼) ref 18; (◆, ◇) ref 19; (△) ref 21, (initiated by BPO, $2f = 1$, 2% in toluene).

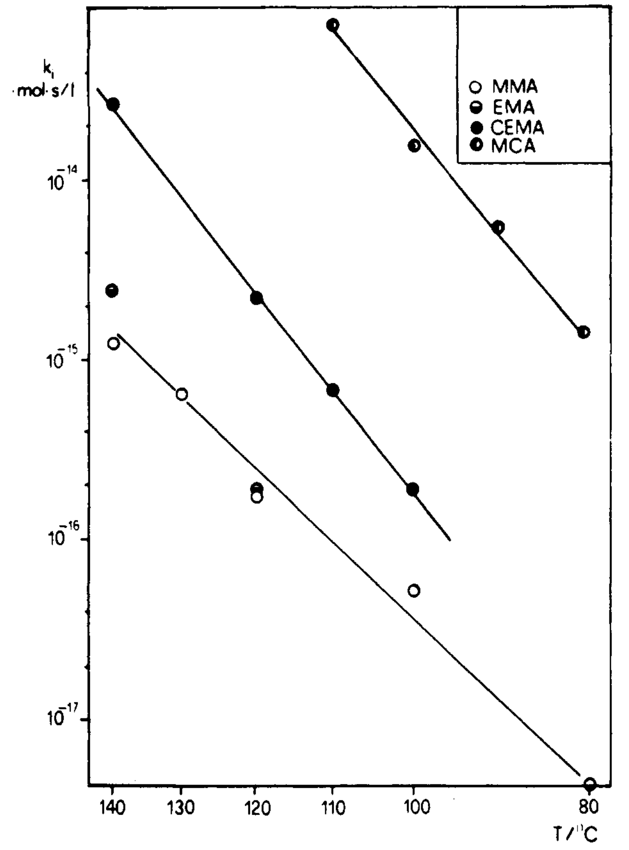

Figure 2. Arrhenius plot for the initiation constant of the spontaneous polymerization.

Table VI
Comparison of Heat of Polymerization Calculated from the Activation Energy with Literature Values

	E_a, kJ/mol	ΔH_{polymn}, kJ/mol	
		from k_i	lit.[28]
MMA	138	−56	−56
CEMA	158	−46	
MCA	148	−51	
β-hydroxyethyl methacrylate			−50
isoprene			−75
chloroprene			−68

According to Flory[23] and Stickler,[24] the E_a values directly correspond to the ΔH^* values for the formation of the biradical as calculated according to Hess. Analogously, the calculation of ΔH_{polym} for the monomers is possible on the basis of the E_a values. The results are given in Table VI together with values available in the literature. As for the electronically similar HEMA, CEMA yields a reasonably smaller ΔH_{polym} than MMA. The effect of chlorine substitution for the methyl group in MMA parallels the effect of the same procedure on isoprene.

2. The probability for a once-formed biradical to initiate the polymerization is determined by the ratio of the rate of reactions yielding species able to propagate or initiate

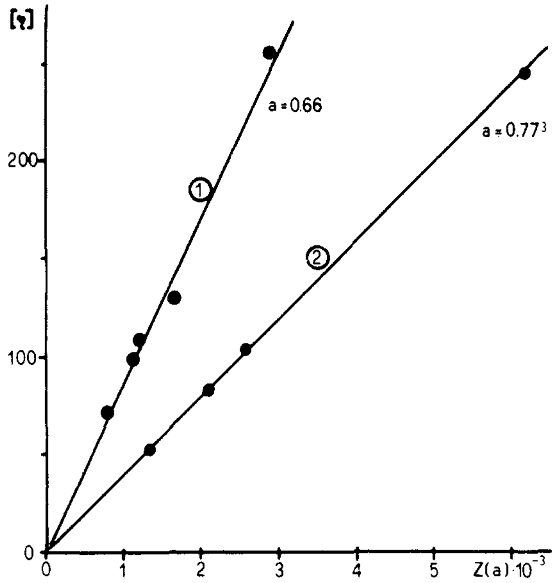

Figure 3. Plot of the Staudinger indices vs. $Z(a_\eta)$ (cf. eq 1) for the optimized value a_η: (1) control experiment, PMMA; (2) PCEMA in THF at 25 °C.

and the rate of self-termination reactions. This ratio is nearly temperature independent, since E_a for the self-termination reaction is about 20 kJ/mol, while the intersystem crossing reaction, which according to ref 7 should be the main initiation path, is temperature independent. Thus to a first approximation the preexponentials A of the Arrhenius plot give a direct measure for the internal heavy-atom effect. The effect of chlorine substituents on this reaction step is very pronounced. The vicinity of the heavy atom to the radical position seems to be of importance (A(MCA) > A(CEMA)). On the other hand, the rather high A value of CEMA might be due to a sterically advantageous six-membered-ring structure.

Molecular Weight Determinations of PCEMA and PMCA

PCEMA. Molecular weights of PCEMA were determined by light scattering, viscometry, and GPC. In its solution properties, PCEMA does not differ strongly from PMMA; i.e., molecular weights can be determined in the same solvents as for PMMA. Since no literature data or narrow-distribution standard samples are available for this polymer, which could be used for the calibration of the GPC and viscometry, the combination of the results of broad-distribution samples in two of the above methods at a time was necessary.

Cane and Capaccioli[25] determined a series of Kuhn–Mark–Houwink parameters by combining GPC and viscometry measurements of broad-distribution samples and compared these with literature data. Assuming the validity of the universal calibration approach, they obtained

$$[\eta]_w = K^{1/(+a_\eta)}\frac{\sum J_i^{a_\eta/(a_\eta+1)}H_i}{\sum H_i} = K^{1/(1+a_\eta)}Z(a_\eta) \qquad (1)$$

where $[\eta]_w$ is the Staudinger index resulting from the viscometry experiment, H_i is the height of the GPC signal at the universal calibration value

$$J_i = M_i[\eta_i] \qquad (2)$$

and K and a_η are the Kuhn–Mark–Houwink parameters. By numeric variation of a_η, applying a Fibonacci routine, the straight line through the origin with the smallest variance is determined. Figure 3 shows the plot of the optimized data. A control experiment using broad-distribution PMMA samples in THF yielded a_η = 0.66 and K = 0.0175; narrow-distribution standard calibration resulted in a_η = 0.688 and K = 0.0130. Thus for $[\eta]_w$ = 100, the values of M_η differ by about 10%. Values for PCEMA are a_η = 0.77$_3$ and K = 0.0033.

A second method to determine the Kuhn–Mark–Houwink parameters combines viscometry and light scattering results. In this case the weight-average molecular weights of the light scattering measurements must be transferred to viscosity-average values, a procedure which is easily performed when the molecular weight distribution and the a_η value are known.[26] From the GPC experiments (cf. Table VII) it is known that as for PMMA the samples polymerized spontaneously have a Schulz distribution with U = 1 (radical polymerization; molecular weight determined by transfer reactions only). a_η can be calculated by iteration; a good starting value is the value of the above method. The result of this procedure, a_η = 0.76 and K = 0.0042, nearly equals the result of the first procedure for PCEMA. The formula $[\bar{\eta}]_w = 3.5 \times 10^{-3}\bar{M}_\eta^{0.77}$ with average values for a_η and K (THF, 25 °C) was taken to calibrate the GPC and to obtain the results of Table VII.

Table VII
Molecular Weights and Transfer Constants of Samples Polymerized Spontaneously

monomer	temp, °C	$\bar{M}_w \times 10^{-6}$	U	$10^5 C_M$	remarks
EMA	140			7.7	[η] in MEK
	120			4.8	[η] in MEK
CEMA	140	4.0		7.43	
	130	4.6	1.1	6.46	
	120	7.2	0.8	4.13	
	110	11.8	0.9		
			1.2	2.52	
	100	14.4	1.1	2.06	
	60			0.26	init polymn
MCA	120	8.1		2.96	
	110	16.2			
		15.8			
		13.9			
		12.7		1.53	
	100	33.7		0.71	
	90	>40			

PMCA. The choice of solvents for PMCA is very limited: only DMF and Me_2SO led to a complete dissolution of the polymer. Because of the high molecular weights, GPC measurements were not possible; the viscometric results were obtained in a gradient viscometer[28] and extrapolated to $G \rightarrow 0$. From the viscometry and light scattering results, a_η = 0.74 and K = 0.0066 were obtained for DMF as solvent at 25 °C. Due to the high molecular weights, these values are less accurate than the PCEMA data.

Transfer Constants

Table VII gives the molecular weights determined for samples polymerized spontaneously at various temperatures. Assuming the termination term in the Mayo equation to be neglegible (for PMCA at 110 °C: $3.3 \times 10^{-7}/\lambda$), the following Arrhenius parameters are obtained for the transfer constants to monomer:

monomer	$\ln C_M =$	$C_{M,100\,°C} \times 10^5$	E_a, kJ/mol
MMA	$-0.255 - 3765/T$	3.2	31.3
EMA	$-0.026 - 3902/T$	2.8	32.4
CEMA	$4.85 - 5883/T$	1.8	48.9
MCA	$15.95 - 10395/T$	0.68	86.2

The results clearly show that transfer effects according to ref 6 cannot be responsible for the reasonably different behavior of chlorine-containing monomers in the spontaneous polymerization.

For MCA, a slight rise of $\bar{M}_w$ with increasing conversions is found, which, at 110 °C, may be explained by transfer to polymer with $C_p = 5 \times 10^{-4}$ per monomer unit (i.e., non end group). For CEMA, transfer constants to some solvents were also determined.

solvent	$C_s^{60\,°C}$
CCl_4	3.27×10^{-5}
$CHBr_3$	1.68×10^{-4}
C_6H_5SH	232

Conclusions

The results presented in this paper show that besides the external heavy-atom effect by solvents or inert gas on the spontaneous polymerization of MMA discussed in the previous paper, an internal effect by chlorine substitution can be observed. As in the spectroscopy of naphthalenes (Table I), the internal effect is much more pronounced.

The reaction orders, the dependence on the atomic number of the heavy-atom included internally or externally, and the parallels to the spectroscopic results strongly support the interpretation of a heavy-atom catalysis of intersystem crossing. This implies that the multiplicity change of the originally formed singlet biradicals is of reasonable importance for the initiation step of the polymerization of MMA and related compounds.

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Registry No. Methyl α-chloroacrylate, 80-63-7; β-chloroethyl methacrylate, 1888-94-4; poly(β-chloroethyl methacrylate), 26937-47-3; methyl methacrylate, 80-62-6; ethyl methacrylate, 97-63-2; poly(ethyl methacrylate), 9003-42-3; poly(methyl α-chloroacrylate), 25704-33-0.

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Hydrophilic Polyurethane Networks Based on Poly(ethylene oxide): Synthesis, Characterization, and Properties. Potential Applications as Biomaterials[†]

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ABSTRACT: Hydrophilic polyurethane networks have been synthesized by step growth polymerization between poly(ethylene oxide) precursor polymers and suitable aliphatic or aromatic pluriisocyanates. The reactions have been carried out in organic solvents such as dioxane. The quantitative exchange between dioxane and water yields optically transparent hydrogels of high hydrophilicity exhibiting improved mechanical properties. The final structure of the networks and their ultimate properties depend upon several parameters such as the type of the pluriisocyanate used, the number-average molecular weight, and the concentration of the precursor poly(ethylene oxide) as well as its polydispersity. The solvent, the temperature, and the catalysts influence considerably the rate and the total duration of the process. The networks obtained are characterized by their equilibrium swelling degrees in dioxane and in water and by their elastic moduli arising from uniaxial compression measurements. In most cases, the materials obtained are optically perfectly transparent, highly hydrophilic with satisfactory mechanical properties, and therefore suitable as potential biomaterials.

Introduction

The numerous methods which have been developed to synthesize hydrophilic polymer networks can be classified into three groups: (1) methods involving free radical copolymerization of two monomers, one of them being biunsaturated and present in small proportions (e.g., 2-hydroxyethyl methacrylate (HEMA) and ethylene dimethacrylate (DME)[1-4]); (2) methods involving graft copolymerization (e.g., graft copolymers of poly(HEMA) onto poly(vinylpyrrolidone)[5] or poly(vinylpyrrolidone) onto silicone rubber[6]); and (3) methods involving step growth polymerization between preexisting linear polymer chains and an appropriate functional reagent (e.g., reaction between an α,ω-dihydroxy polymer and a pluriisocyanate[7]

[†] Dedicated to Professor W. H. Stockmayer on the occasion of his 70th birthday in grateful recognition and with best regards.