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THE POLYMERIZATIONS OF *N*-METHYL-*N*-PHENYL-2-AMINOETHYL METHACRYLATE AND 4-DIMETHYLAMINOSTYRENE INITIATED WITH CARBOXYLIC ACIDS

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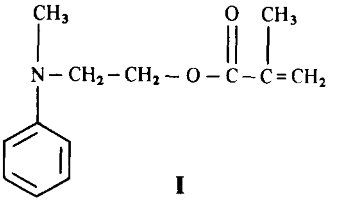
Abstract—By using the copolymerizations of *N*-methyl-*N*-phenyl-2-aminoethyl methacrylate (**I**) and 4-dimethylaminostyrene (**II**) with styrene initiated with 2,2'-azoisobutyronitrile (AIBN) and with CCl_3COOH, the copolymerization parameters and Alfrey-Price copolymerization constants e and Q were determined for **I** and **II**. The only product of polymerizations initiated with CCl_3COOH and CH_3COOH in mixtures of **II** with vinyl monomers was a homopolymer of **II**. The order of homopolymerization of **II** in benzene initiated with CCl_3COOH at 50° was 0.99 with respect to [**II**] and 1.10 with respect to [CCl_3COOH]; the temperature dependence of homopolymerization in the range 25–40° was $63 \pm 5\ \text{kJ mol}^{-1}$. The rate of homopolymerization of **II** in solution in C_6H_6 at 50° was virtually unaffected by inhibitors. In the polymerization initiated with carboxylic acids, the radical character of propagation centres was proved for **I**, but not for **II**.

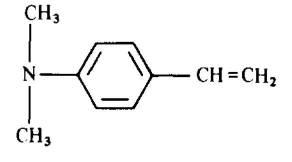
INTRODUCTION

In the homopolymerizations of *N*-methyl-*N*-phenyl-(2-aminoethyl) methacrylate (**I**) and 4-dimethylaminostyrene (**II**) initiated with carboxylic acids, the efficiency of inhibitors of radical polymerization was low [1]. In the case of **I** their effect became distinct only at concentrations $> 2 \times 10^{-3}$ M, while the polymerization of **II** still proceeded at an almost unreduced rate at a benzoquinone concentration of $5 \times 10^{-3}\ \text{mol dm}^{-3}$. In the polymerization of **I**, noting the effectiveness of inhibitors of radical polymerization, the acrylate type of the monomer and the presence of carboxylic acid, one can rule out ionic character for the polymerization but further characteristics are necessary in order to elucidate its course. In the case of **II**, a cationic mechanism of polymerization cannot be *a priori* ruled out.

In this study the relative reactivities of **I** and **II** towards other monomers were investigated in polymerizations initiated both with AIBN and with carboxylic acid. The temperature dependence of homopolymerization of **II** and the orders of homopolymerization of **II** with respect to carboxylic acid and the monomer were also determined.



I



II

EXPERIMENTAL

Chemicals

The characteristics of initial compounds have been described [1]. The solvents were rectified on a Bruun's column (32 TP) and were chromatographically pure.

Methods

Purities of liquid components were checked with a gas chromatograph Chrom 3, Laboratory Instruments, Prague. All polymerizations were performed in sealed glass dilatometers, *ca.* 8 cm^3 or 4 cm^3 in volume, in an inert atmosphere. The copolymerizations styrene (S)—**I** initiated with 0.02 M AIBN or 0.05 M CCl_3COOH, S-**II** initiated with 0.01 M AIBN and attempts to copolymerize **II** with S, acrylonitrile (AN), methacrylic acid (MAA), methyl methacrylate (MMA) and α-methylstyrene with CCl_3COOH or CH_3COOH as initiators were carried out in benzene solution at 50° and with total monomer concentration 4 M. The initial concentrations of comonomers are expressed through the mol fraction of styrene (F_0) in Table 1. The conversions of comonomers did not exceed 10% by mass. From the copolymerization mixtures without acids, the copolymers S-I and S-**II** were precipitated with ethanol containing a small amount of NH_4Cl accelerating the aggregation of the polymer; all samples were dried in vacuum to constant mass. The specific contraction corresponding to the conversion of 1 g of comonomers into polymer was calculated from the mass of the copolymers and the volume contraction of the given polymerization mixture. The copolymers were reprecipitated from benzene solutions using the precipitant mentioned above, and dried. Carbon and nitrogen contents of the copolymers were determined by elemental analysis; the limiting viscosity number in benzene solution at 20° was determined with an Ubbelohde viscometer, and the number-average degree of polymerization in benzene solution was determined using a membrane osmometer (Hallikainen, model 1361 DS4) or a

Table 1. Copolymerization of styrene(S)—*N*-methyl-*N*-phenyl-2-aminoethyl methacrylate (**I**) and S—4-dimethylaminostyrene (**II**) initiated with AIBN and CCl_3COOH in benzene solution at 50°

S-**I** (0.02 M AIBN)			S-**I** (0.05 M CCl_3COOH)			S-**II** (0.01 M AIBN)			
F_0	f	$W \cdot 10^5$ (sec^{-1})	F_0	f	$W \cdot 10^5$ (sec^{-1})	F_0	f	$W \cdot 10^5$ (sec^{-1})	$[\eta]$ ($cm^3 g^{-1}$)
0.288	0.334	1.83	0.285	0.309	1.04	0.241	0.299	0.21	40
0.347	0.370	1.95	0.348	0.391	—	0.409	0.459	0.24	48
0.410	0.403	0.72	0.402	0.429	0.79	0.520	0.560	0.25	49
0.451	0.443	1.10	0.445	0.464	0.59	0.606	0.645	0.27	45
0.602	0.539	1.00	0.493	0.458	0.51	0.671	0.692	0.26	44
0.637	0.577	0.85	0.552	0.512	0.46	0.699	0.726	0.27	47
0.675	0.602	0.74	0.600	0.559	0.43	0.732	0.747	0.26	47
0.718	0.632	0.48	0.639	0.570	0.44	0.754	0.758	0.24	52
			0.664	0.591	0.36				
			0.716	0.626	0.38				

F_0 and f—mol fractions of styrene in the initial mixture of monomers and in the copolymer respectively; W—ratio of the polymerization rate (R_p) in $Msec^{-1}$ to the overall concentration of comonomers expressed in M.

* In C_6H_6 at 20°.

VP osmometer (Hitachi–Perkin–Elmer, model 115). The compositions of copolymers S-**I** and S-**II** were determined from the carbon and nitrogen contents respectively. The copolymerization parameters were calculated from the compositions of copolymers using the Joshi–Joshi [2] and Fineman–Ross [3] methods; the Alfrey–Price constants [4] were determined from these parameters, assuming that for S, $e = -0.8$ and $Q = 1.0$. The specific contractions were used to recalculate the determined "Volume contraction–Time" dependences to "Conversion–Time" dependences, and the values thus obtained were used to calculate the initial rate of copolymerization in $Msec^{-1}$ at a known composition of the copolymer [5].

The initial monomer concentration in benzene in the determination of the temperature dependence of homopolymerization of **II** initiated with CCl_3COOH was 2 M. The polymerizations of **II** were interrupted at a known contraction; the polymerization mixtures were shaken with an aqueous solution of ammonia and benzene was removed at reduced pressure after stabilization with hydroquinone. The polymer was precipitated with hexane from the viscous residue, and dried to constant mass. The final volume contractions and the amounts of poly(**II**) obtained were used to calculate the specific contractions at various temperatures. The volume contractions during the homopolymerization of **II** were recalculated to the amount of poly(**II**) formed by using these specific contractions ($^\circ/cm^3 g^{-1}$): 20/0, 0992; 30/0, 1076; 40/0, 1155; 50/0, 1233.

RESULTS AND DISCUSSION

Copolymerization of S-I and S-II

Table 1 shows the mol fractions of basic styrene units (f) in the increments of copolymers formed in the copolymerization of S-**I** and S-**II** with F_0 mol fractions of S. The W values give the ratio of the polymerization rate (R_p) in $Msec^{-1}$ and the overall molar concentration of comonomers. Using the Fineman–Ross equation [3], the copolymerization parameters r_1, r_2 were calculated from Eqn (1):

$$\Phi_0 - (\Phi_0/\varphi) = r_1(\Phi_0^2/\varphi) - r_2 \qquad (1)$$

by substitution of the initial molar ratio of both comonomers ($[S]/[I])_0$ or of the ratio of basic units in the increment of the copolymer ($d[S]/d[I]$) for Φ_0, and φ, and also by the substitution of the reciprocal values of these ratios, i.e. ($[I]/[S])_0$ or ($d[I]/d[S]$) for Φ_0 and φ. For the latter case, the parameters in Table 2 are given in brackets. The differences between the "reciprocal" parameters thus calculated are less than 0.055, and their average values are almost identical with the parameters calculated by the Joshi–Joshi method [2]. Average values according to Fineman–Ross and Joshi–Joshi are given as the resulting copolymerization parameters. For the copolymerizations of S-**I** initiated with AIBN and CCl_3COOH, the copolymerization parameters are virtually identical. Using the copolymerization parameters determined for the copolymerization S-**I** initiated with AIBN ($r_1 = 0.43$; $r_2 = 0.58$), the copolymerization diagram was constructed as represented by the solid line in Fig. 1. Experimental points, i.e. the determined composition of the copolymer, are denoted with circles for AIBN and with crosses for CCl_3COOH as the initiators. The agreement between experimental points and the calculated diagram confirms the radical character of propagation centres formed by interaction between CCl_3COOH and **I**; the radical course of copolymerization was suggested [1] by the 0.5 order of the homopolymerization of **I** with respect to $[CCl_3COOH]$, but seemed dubious due to the low sensitivity of this system towards inhibitors. The copolymerization parameters and the mol fraction of the azeotropic polymerization mixture ($F_{0(az)}$) indicate that both radicals are more reactive with respect to the other monomer than to their own, and that the rate of addition of molecules **I** to the radical chain is higher than that of molecules S; this is obviously also the reason why the values of W decrease with increasing F_0. The Alfrey–Price constants e and Q calculated for **I** from the copolymerization parameters are close to the values for ethyl methacrylate ($e = 0.52$; $Q = 0.73$). The considerably different e values for S (-0.8) and **I** account for the tendency for alternation in the propagation reaction ($r_1r_2 < 0.25$).

A check on the copolymerization parameters of S-**II**, $r_1 = 1.015$, $r_2 = 0.84$ [6] and $r_1 = 0.82$, $r_2 = 0.58$ [7] determined earlier was justified, because the first measurement was carried out with benzoyl peroxide as initiator when its radical reaction with tertiary amines [8] was still unknown, while in the

Table 2. Characteristics of copolymerization of **S-I** and **S-II** according to data in Table 1

Characteristics	**S-I** (0.02 M AIBN)	**S-I** (0.05 M CCl_3COOH)	**S-II** (0.01 M AIBN)
r_1^*	0.445 (0.412)	0.411 (0.464)	0.944 (0.979)
r_2^*	0.592 (0.557)	0.520 (0.575)	0.612 (0.659)
r_1; r_2^{**}	0.438 ± 0.02; 0.584 ± 0.02	0.428 ± 0.03; 0.535 ± 0.04	0.975 ± 0.03; 0.653 ± 0.02
r_1; r_2^{β}	0.43 ± 0.02; 0.58 ± 0.02	0.43 ± 0.03; 0.54 ± 0.04	0.97 ± 0.03; 0.64 ± 0.02
e_2; Q_2; $F_{0(az)}$	0.37 ± 0.04; 0.90 ± 0.04; 0.424	0.41 ± 0.06; 0.88 ± 0.02; 0.447	−1.48 ± 0.08; 1.77 ± 0.04; 0.923

$F_{0(az)}$ corresponds to F_0 in an azeotropic polymerization mixture; * and ** according to the Fineman–Ross and Joshi–Joshi methods respectively.

† Mean value.

second measurement the parameters were calculated using the Fineman–Ross method from only five copolymerizations. Table 2 shows that the resulting copolymerization parameters lie in the range of earlier values [6, 7]. The resulting constants e and Q for **II** are close to their values for S (−0.8 and 1.0). For this reason, the reactivities of both comonomers towards the radicals do not differ greatly and W is virtually independent of F_0. Since in the initiation of homopolymerization of **I** and **II** with carboxylic acids [1], $[\eta]$ of poly(**II**) appeared to be lower by an order of magnitude than $[\eta]$ of poly(**I**), values of $[\eta]$ were now measured for poly(**II**) prepared with AIBN. Their independence of F_0 indicates that in the absence of carboxylic acid neither comonomer **II** nor its basic unit in the polymer affects the degree of polymerization.

According to the elemental analyses, the only product of polymerizations initiated with carboxylic acids in mixtures of **II** with vinyl monomers was always the homopolymer of **II**. Figure 2 shows the course of such polymerizations initiated with CCl_3COOH in benzene solutions at 50°; the measured contractions were recalculated only to the percent of polymerized **II**. It has been observed that **II** homopolymerizes relatively quickly and up to a high conversion in the presence of MAA; obviously, MAA initiates and affects the chain propagation similarly to CH_3COOH, which is less effective than CCl_3COOH [1]. In the presence of the other vinyl compounds, the polymerization rapidly slows down with time, probably because of the fast consumption of CCl_3COOH. The very low $[\eta]$ values of isolated homopolymers **II** (with AN 1.2, with MAA 1.5 and with S 2.7 $cm^3\,g^{-1}$) are similar to those for homopolymers **II** obtained with CH_3COOH [1] as the initiator and much lower than $[\eta]$ of copolymers S-**II** obtained with AIBN (Table 1). Again, only the homopolymer of **II** was produced in polymerization proceeding at room temperature in a solution of 2 M of S and 2 M of **II** in acetic acid. After 30 min reaction, 53% poly(**II**) with $[\eta] = 0.8\,cm^3\,g^{-1}$ was isolated.

*Characteristics of the homopolymerization of **II** initiated with CCl_3COOH and CH_3COOH*

The rate of homopolymerization of **II** in benzene initiated with 0.05 M CCl_3COOH at 50° increased with the molar concentration of **II** thus ($R_p \times 10^4$ in $Msec^{-1}$/[**II**]): 1.02/1.08; 0.92/1.21; 1.28/1.33; 1.39/1.60; 2.01/2.35; 2.71/3.08. The reaction order with respect to [**II**] from these data is 0.99. The $[\eta]$ values of the polymers ranged between 3 and 4 $cm^3\,g^{-1}$.

At a fixed concentration of 2 M **II** in benzene solution and at 40°, the order of homopolymerization of **II** was determined with respect to [CCl_3COOH]. The time (min) needed for 3% conversion of **II** to the polymer decreased with increasing concentration of CCl_3COOH as follows ([CCl_3COOH] × 10^3/min): 5/161; 7/117; 10/82; 20/32. The slope calculated from the dependence of log min^{-1} on log [CCl_3COOH], i.e. the polymerization order of **II** with respect to [CCl_3COOH], is 1:1.

The temperature dependence of the rate of polymerization of 2 M **II** initiated in benzene solution with 0.02 M CCl_3COOH was determined at 25, 30, 35 and 40°. The time (min) needed for 3% conversion of **II**

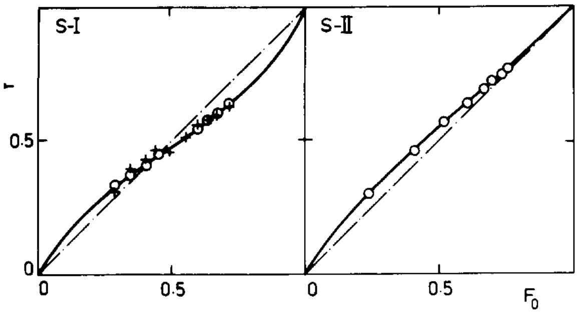


Fig. 1. Copolymerization diagrams calculated (——) from the determined copolymerization parameters. F_0 and f are the mol fractions of styrene in the initial mixture of monomers and in the copolymer respectively; (○) and (+) are the determined compositions of the copolymer after initiation with AIBN and CCl_3COOH respectively.

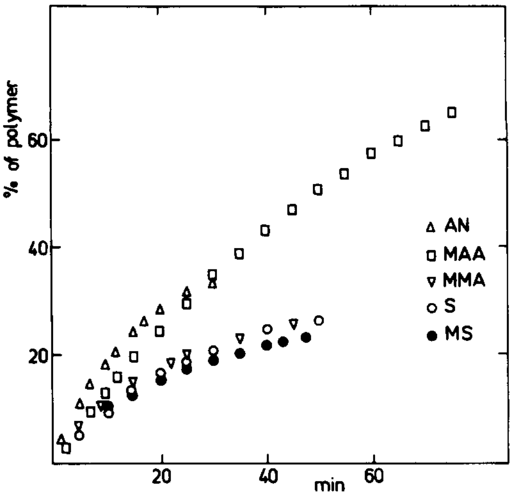
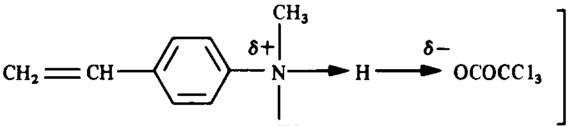


Fig. 2. Polymerization of **II** (2 M), vinyl compound (2 M) and CCl_3COOH (0.05 M) in benzene solutions at 50°; AN—acrylonitrile, MAA—methacrylic acid, MMA—methyl methacrylate, S—styrene, MS—α-methylstyrene.

decreased with increasing temperature thus: (°/min): 25/101; 30/63; 35/43; 40/28. The overall activation energy of copolymerization of **II**, calculated from the dependence of log $\min^{-1}$ on $1/T$ is 63 ± 5 kJ mol^{-1}; the value determined earlier for the polymerization of **II** with CH_3COOH [1] is $E_g = 53.7$ kJ mol^{-1}.

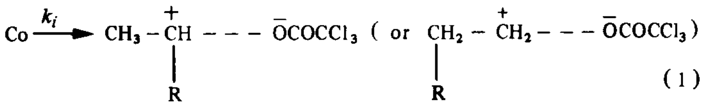
The polymerization of 2 M **II** initiated in benzene solution at 30° with 0.05 M CCl_3COOH was not affected by inhibitors of radical reactions. When 0.005 M BQ or 2,2-diphenyl-1-picrylhydrazyl (DPPH) were used or the reaction mixture was saturated with oxygen, the following percentage of polymer with the respective limiting viscosity number was reached (%/[η] in $cm^3\,g^{-1}$): without inhibitor 6.6/3; BQ 6.8/5; DPPH 6.5/5; O_2 7.6/2. Picric acid (0.005 M) also was ineffective in the homopolymerization of 2 M **II** in benzene solution at 50° in the presence of 2 M CH_3COOH. Within 120 min, the polymerization without this acid proceeded to a 67% conversion; in its presence, the conversion was 88%.

While [η] of poly(**II**) prepared by the polymerization of 2 M **II** in benzene solution with 0.02 M AIBN at 65° was 12.5 $cm^3\,g^{-1}$, the polymerization of 2 M **II** in C_6H_6 with CH_3COOH and CCl_3COOH as initiators at temperatures below 50° gives rise to polymers with $[\eta] < 5\,cm^3\,g^{-1}$ and $\bar{P}_n < 50$. Spectrometry (i.r.) and chemical analysis of these polymers did not reveal acyl moieties or chlorine. The fact that no dependence of [η] on the concentration of **II** and CCl_3COOH could be detected suggests that $\bar{P}_n$ is predominantly determined by chain transfer, probably to monomer. The ineffectiveness of inhibitors of radical reactions and the inertia of the investigated vinyl monomers in the polymerization of **II** initiated with carboxylic acids suggest a possible cationic polymerization mechanism. An increased tendency of **II** to cationic activation is indicated by the high electron density on its vinyl bond, expressed through the low copolymerizations constant e (Table 1). A cationic type of polymerization of **II** was also assumed in the initiation with chloranil [9]. Since in the initiation with CCl_3COOH the molar concentration of **II** was at least 40 times higher, the acid in the system was not free but was bound to **II** as a "complex" which is not regarded [10–12] as a pure molecular compound or a pure salt. It can be represented as



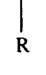
(Co)

With respect to the positive overall activation energy of polymerization of **II** initiated with CCl_3COOH, it can be assumed that the transformation of the complex into an active cationic centre requires the overcoming of a considerable energy barrier. The reaction centre thus formed (C^*) may then add a monomer molecule of **II**, may be transferred to monomer or may be monomolecularly deactivated according to scheme 3 ($R = -C_6H_4N(CH_3)_2$):

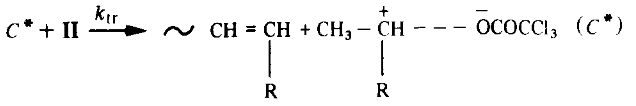


$$\mathrm{Co} \xrightarrow{k_i} \mathrm{CH_3}-\overset{+}{\underset{\substack{|\\ \mathrm{R}}}{\mathrm{CH}}}---\bar{\mathrm{O}}\mathrm{COCCl_3}\ (\text{ or }\ \underset{\substack{|\\ \mathrm{R}}}{\mathrm{CH_2}}-\overset{+}{\mathrm{CH_2}}---\bar{\mathrm{O}}\mathrm{COCCl_3}) \qquad (1)$$

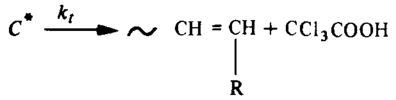
(C^*)



$$C^* + \mathrm{II} \xrightarrow{k_p} \sim \mathrm{CH_2}-\overset{+}{\underset{\substack{|\\ \mathrm{R}}}{\mathrm{CH}}}---\bar{\mathrm{O}}\mathrm{COCCl_3}\ (C^*) \qquad (2)$$



$$C^{*} + \mathrm{II} \xrightarrow{k_{tr}} \sim \mathrm{CH}=\underset{\mathrm{R}}{\mathrm{CH}} + \mathrm{CH_3}-\underset{\mathrm{R}}{\overset{+}{\mathrm{CH}}} --- \overset{-}{\mathrm{O}}\mathrm{COCCl_3}\ (C^{*}) \qquad (3)$$



$$C^{*} \xrightarrow{k_t} \sim \mathrm{CH}=\underset{\mathrm{R}}{\mathrm{CH}} + \mathrm{CCl_3COOH} \qquad (4)$$

If $[\mathrm{CCl_3COOH}]_0 \ll [\mathrm{II}]_0$, the concentration of the complex can be expressed [1] by the equation

$$[\mathrm{Co}] \doteq \mathrm{K}'[\mathrm{CCl_3COOH}]_0(\mathrm{K}' + 1)^{-1} \qquad (5)$$

in which $\mathrm{K}' = \mathrm{K}([\mathrm{II}]_0 - [\mathrm{Co}])$, K is the equilibrium constant for complex formation and the zero subscript denotes the initial concentrations. Assuming a stationary state, the equation

$$R_p = k_p k_i k_t^{-1}\mathrm{K}'(\mathrm{K}' + 1)^{-1}[\mathrm{CCl_3COOH}]_0[\mathrm{II}]_0 \qquad (6)$$

can be derived for the initial polymerization rate, in agreement with the experimentally determined orders of polymerization with respect to $[\mathrm{CCl_3COOH}]$ and $[\mathrm{II}]$.

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