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Copolymerization of Styrene with *N*-Arylmaleimides

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ABSTRACT: The copolymerization of styrene with (2-chlorophenyl)maleimides was investigated in two solvents. It has been shown that a charge-transfer complex participates in the process of copolymerization. The relative reactivity ratios were found to be solvent-dependent. The initial rate of copolymerization was measured as a function of the monomer molar ratios, and the participation of the charge-transfer complex monomer and the free monomers was quantitatively estimated.

Introduction

In continuation of our interest in investigating the polymerization behavior of the *N*-arylmaleimides,[1-3] styrene was chosen as a comonomer to study their copolymerization behavior. There has been controversial information regarding the copolymerization of *N*-phenylmaleimide (NPMI) and styrene (St).

It was shown that NPMI and St undergo alternating copolymerization in benzene and in chiral solvents;[4,5] however, trials to detect the formation of complexation between the monomers with UV and/or NMR spectroscopy were not successful. On the other hand, Russian reporters have indicated[6,7] that the copolymerization proceeded via the participation of a charge-transfer complex (CTC) in addition to free monomers and that the predominant mechanism was by the addition of CTC monomer to the macroradical. No detailed information is however available.

The large difference in polarity between *e* values for St ($e = -0.8$) and *N*-arylmaleimide (e.g., *N*-(2-chlorophenyl)maleimide[2,4]) seemed a good enough base for the formation of even a weak CTC between these two monomers. This study attempts to throw more light on this controversial behavior.

Several approaches have been used in the literature to treat the kinetic data of systems with the anticipated participation of CTC in the copolymerization process. Seiner and Litt[8] first derived a mathematical formulation for alternating copolymerization systems. In view of the complexity of the mathematical expressions, they were used under certain restrictions, in most cases not representing the real situation. Farmer et al.[9,10] have analyzed the model in terms of kinetic probabilities and have been able to compare the importance of different models in a few complicated systems. Braun and Czerwinski[11] extended the method of Farmer et al. to describe the kinetic relationship for systems supposed to involve complexes between monomers.

Arnaud, Caze, and Fossey[12] and independently Georgiev and Zubov[13] have used the existence of maxima in the rate vs. feed composition curve in alternating copolymerization in order to analyze the kinetic data and to get values for the different rate constants. However, the exact position of the maxima is usually not well-defined, and the method cannot be applied always with certainity.

A treatment of the data for alternating copolymerization was also proposed by Shirota et al.[14,15] The treatment is based on the view that a 1:1 alternation in the resulting copolymer is brought about by the stabilization of the transition state in the cross reactions of the free monomers and the complex. The treatment of Shirota et al. has been adapted by us in the present study.

Recently, Deb and Meyerhoff[16,17] presented a scheme for the copolymerization of styrene and maleic anhydride that included the participation of a charge-transfer complex between monomers in the propagation. They derived an equation for the rate of copolymerization that is resolvable into two parts signifying the influence of propagation via free monomer and by complex.

Experimental Section

Monomers. *N*-(2-Chlorophenyl)maleimide (2CMI) was prepared by the method of Searle[18] and recrystallized several times from ethanol. The purity of 2CMI was checked by TLC and NMR in order to make sure that it was free from unreacted maleic anhydride and the uncyclized maleamic acid. The latter acts as a moderate inhibitor for free radical polymerization of the maleimide. Melting points and elemental analysis agreed well with literature values.[1,4]

Styrene was distilled under reduced pressure after removal of the inhibitor by the usual method. It was kept cold and redistilled again directly before use.

Solvents. Dioxane (BDH) was refluxed over sodium wire for 24 h and distilled before use. DMF (prolabo) was used as received. Chloroform, methanol, ethanol, and acetone, pure for analysis (Fluka), were distilled before use.

Initiator. 2,2-Azobis(isobutyronitrile) (AIBN) (BDH) was recrystallized twice from methanol.

Rates of Copolymerization and Monomer Reactivity Ratios. Rates of copolymerization were measured dilatometrically. Dilatometers filled with initiator (AIBN), monomer mixture, and solvent were connected to a high-vacuum line and freed of oxygen by three freezing–thawing cycles. The dilatometers were then placed in transparent Dewar s flasks connected to a thermostat. The volume contraction was recorded as a function of time. The reaction was terminated by vacuum suction of the contents and precipitation in excess cold methanol. After filtration and washing, the copolymers were dried under vacuum to constant weight. The conversion was determined gravimetrically. Since

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the volume contraction–time curves were always straight lines (up to the conversion ranges used), the rates were converted into mol L^{-1} min^{-1}.

For the determination of the monomer reactivity ratios, ampules were used. The charged ampules were also freeze–thawed three times, sealed, and placed in the required temperature. The copolymers were precipitated in methanol, filtered, washed, and reprecipitated twice from dioxane in methanol, and finally dried to constant weight.

Copolymer Analysis. Copolymer compositions were calculted by UV spectroscopy. Calibration curves of polystyrene and pol](2CMI) in $CHCl_3$ were constructed at 275 nm, and the molar extinction coefficients of the two polymers at this wavelength were used to calculate the composition of the copolymers.

UV spectra were recorded with a Unicam SP-800 spectrophotometer. ^1H NMR spectra were taken with a WH-90 Bruker spectrometer with Me_4Si as internal standard. For the determination of the equilibrium constants of the complex formation, NMR spectroscopy was used. The concentration of the acceptor (2CMI) was kept constant while the concentration of the donor (St) was increased. Concentrations were determined by weighing each component sequentially in the NMR tube, whose volume was previously calibrated. All measurements were conducted at room temperature (ca. 30 °C).

IR spectra were taken with a Unicam SP 3-200 spectrophotometer.

Results and Discussion

On mixing St with 2CMI no coloration was observed. The UV spectra of different molar ratios of these two monomers in chloroform, dioxane, or cyclohexane revealed the formation of no new independent bands. The Benesi–Hildebrand[19] method for the determination of the equilibrium constant of the expected CTC using UV spectroscopy was then inapplicable. On the other hand, when the procedure of Hanna and Ashbough[20] using NMR spectroscopy was used for the same purpose, definite positive results were obtained. It has been shown by Bryce-Smith and Hems[21] that N-substituted maleimides experience a large upfield chemical shift in benzene solvent, and this was attributed to association of the solute and solvent molecules. In the present study the chemical shifts of the olefinic proton of 2CMI appeared at $\delta(CHCl_3)$ 6.84, δ(dioxane) 6.88, and δ(DMF) 7.14. These data indicate a strong effect of the solvents on the protons of the double bond and, consequently, on the reactivity of the monomer. To determine the equilibrium constant of the CTC between St and 2CMI in these three solvents, the chemical shift of the ethylene proton was monitored as a function of the styrene concentration. A noticeable change of chemical shift on increasing the St concentration was observed in $CDCl_3$. A smaller effect in dioxane and much smaller one in DMF (deuterated solvents) were obtained. Figure 1 presents these data for the three solvents at room temperature.

The lines of Figure 1 were plotted according to the following equation:[8]

$$1/[\mathrm{St}] = (1/\Delta_{\mathrm{obsd}})K\Delta_{\mathrm{com}} - K$$

where K is the equilibrium constant, $\Delta_{\mathrm{obsd}} = \delta^{A}{}_{\mathrm{fr}} - \delta^{A}{}_{\mathrm{obsd}}$, $\Delta_{\mathrm{com}} = \delta^{A}{}_{\mathrm{fr}} - \Delta^{A}{}_{\mathrm{com}}$, $\delta^{A}{}_{\mathrm{fr}}$ is the chemical shift of the free 2CMI, $\delta^{A}{}_{\mathrm{obsd}}$ is the observed chemical shift based on the 2CMI, and $\delta^{A}{}_{\mathrm{com}}$ is the chemical shift of the complexed 2CMI. The intercepts (K) in dioxane and DMF obtained by the least-squares method were zero and a negative value, respectively. A positive K value of 0.84 was obtained in chloroform. The high dielectric constant and polarity of DMF are known to prevent the formation of a stable CTC.[22]

Dioxane, on the other hand, associates with the maleimide, leaving small chance for the formation of CTC with St.

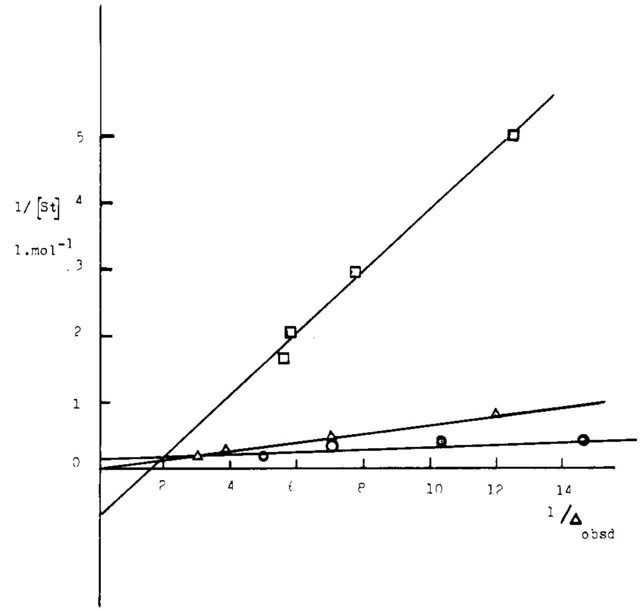

Figure 1. Plot of $1/\Delta_{\mathrm{obsd}}$ vs. $1/[\mathrm{St}]_0$ for the NMR shifts of 2CMI protons using styrene as donor in (□) chloroform, (△) dioxane, and (○) DMF.

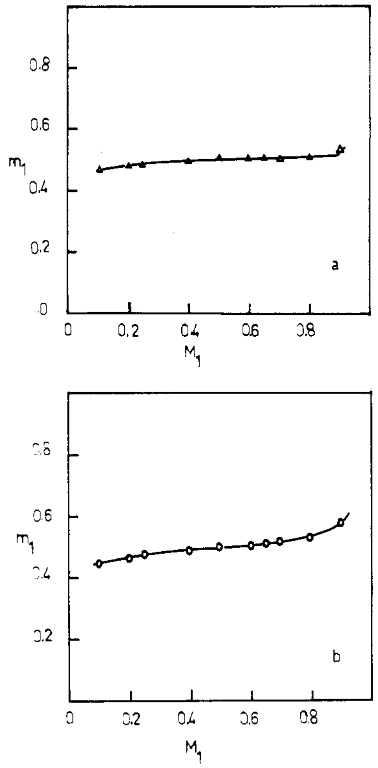

Figure 2. Diagrams for radical copolymerization of 2CMI $[M_1]$ with St $[M_2]$ in (a) chloroform and (b) in dioxane at 60 °C with AIBN as initiator. m_1 is the mole fraction of $[M_1]$ in the copolymer and M_1 is that in the monomer feed composition.

It has been shown previously that the rate of homopolymerization of 2CMI in DMF is lower than in $CHCl_3$ or in dioxane;[1] therefore, DMF was not used for further study in this copolymerization.

The copolymerization of St with 2CMI was investigated both in $CHCl_3$ and in dioxane. The copolymerization diagrams are shown in Figure 2, parts a and b, respectively. A strong tendency for alternation was found in both cases. The reactivity ratios were calculated with the Kelen–Tüdös equations[23,24] as shown in Figure 3

$$\eta = (r_1 + r_2/\alpha)\xi - r_2/\alpha$$

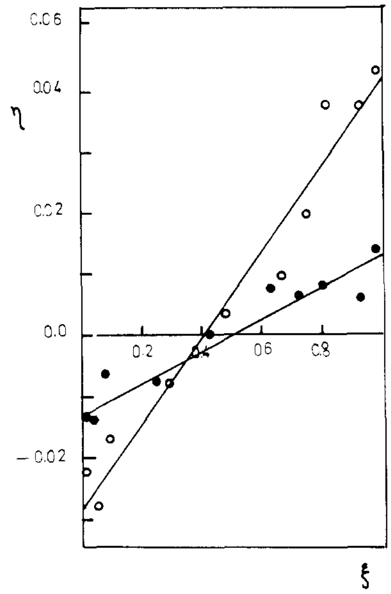

Figure 3. Kelen–Tüdös plots: (●) dioxane; (○) chloroform.

Table I
Copolymerization of Styrene (M_1) and 2CMI (M_2) in Chloroform and Dioxane at 60 °C with AIBN Initiator[a]

no.	monom feed composn $[M_1]$	copolymer composition in $CHCl_3$ m_1	conversion, %	in dioxane m_1	conversion, %
1	0.1	0.462	8.5	0.45	3.2
2	0.2	0.481	12.5	0.469	4.2
3	0.25	0.493	16.2	0.485	6.2
4	0.40	0.495	16.1	0.495	7.2
5	0.50	0.500	12.5	0.502	8.0
6	0.60	0.505	16.0	0.505	9.55
7	0.65	0.504	6.2	0.512	
8	0.70	0.506	16.0	0.525	9.6
9	0.80	0.506	8.0	0.537	10.0
10	0.90	0.531	16.0	0.583	8.23

react. ratios	in $CHCl_3$	in dioxane
r_1	0.0169 ± 0.006	0.0305 ± 0.0077
r_2	0.0126 ± 0.004	0.0415 ± 0.007
r_1r_2	2.1×10^{-4}	1.26×10^{-3}

[a] Total monomer concentration 1 mol L^{-1}; initiator concentration is 2×10^{-2} mol L^{-1}.

where $\eta = G/(\alpha + F)$, $\xi = F/(\alpha + F)$, $G = (y - 1)X/y$, $F = X^2/y$, $y = d[M_1]/d[M_2]$, and $X = [M_1]/[M_2]$. α is a parameter of symmetrization, the optimal value for a given series of measurements being

$$\alpha = (F_{\min}F_{\max})^{0.5}$$

Table I summarizes the experimental data of copolymerization as well as the values of the apparent reactivity ratios. The value of r_2 (2CMI) increases in dioxane over that in chloroform, which could be due to the association of the solvent molecules with the 2CMI growing radicals, rendering the latter more reactive in dioxane than in chloroform. It has been previously shown that the rate of polymerization of 2CMI in dioxane is higher than in chloroform.[1] The higher reactivity in dioxane leads to a lower tendency of alternation in this solvent, as evident from the product r_1r_2 as well as from the copolymerization diagram, especially at higher values of 2CMI in the monomer feed (Figure 2b).

Some Aspects of the Kinetics of Copolymerization. The initial rate of copolymerization R_p was measured as a function of the initiator concentration [I] at constant total monomer concentration $[M_1] = [M_2] = 0.5$ mol L^{-1} in chloroform at 60 °C. Figure 4 illustrates the dependence of R_p on $[I]^{0.5}$. A straight line passing through the origin demonstrates the bimolecular termination of the copolymerization process.

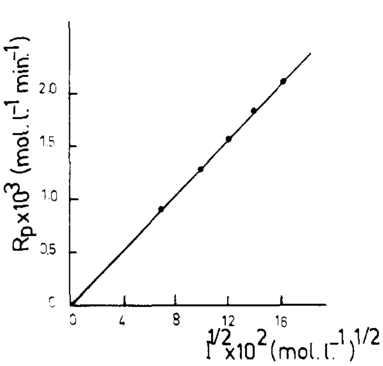

Figure 4. Plot of the initial rate of copolymerization R_p vs. $[AIBN]^{0.5}$ in chloroform at 60 °C: [St] = [2CMI] = 0.5 mol L^{-1}.

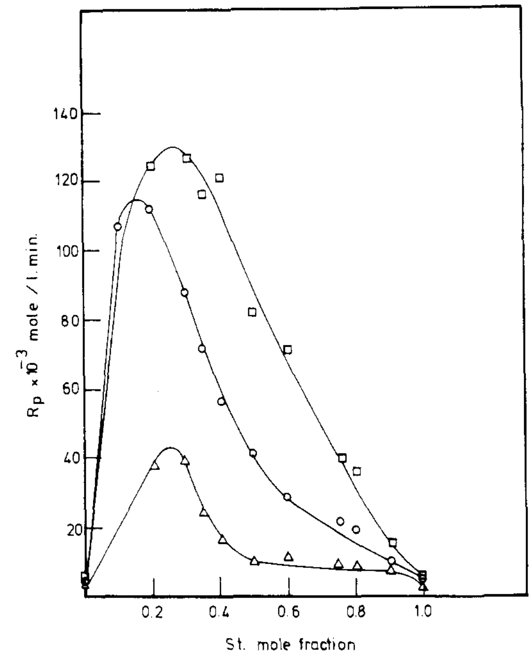

Figure 5. Dependence of the initial rate R_p on monomer feed composition in chloroform at various total monomer concentration T; (△)1, (○)2, and (□) 2.5 mol L^{-1}. [AIBN] = $2.7.10^{-2}$ mol L^{-1}. Temperature = 60 °C.

To illustrate the role of the CTC in the copolymerization, the initial rates were measured for various monomer feed compositions in chloroform at total monomer concentrations of 1.0, 2.0, and 2.5 mol L^{-1} and 0.5, 1.0, and 1.5 mol L^{-1} in dioxane, using [AIBN] = 2.7×10^{-2} mol L^{-1} as intitiator, and are given in Figures 5 and 6, respectively.

The rate R_p does not maximize at the equimolar feed ratio for different total monomer concentrations; there are, however, ill-defined maxima approximately at 80–90 mol % 2CMI in both solvents, which is far away from the equimolar feed composition. The monotonous increase in rate with 2CMI content in the feed suggests propagation via free monomer along with that via complex in both chloroform and dioxane. The rate of copolymerization is higher in dioxane than in chloroform, which is due to the complexation of the maleimide derivatives with dioxane. When the mole fraction of 2CMI exceeded 0.6 in dioxane at a total monomer concentration of 1.5 mol L^{-1}, the contents of the dilatometer polymerized during the thawing

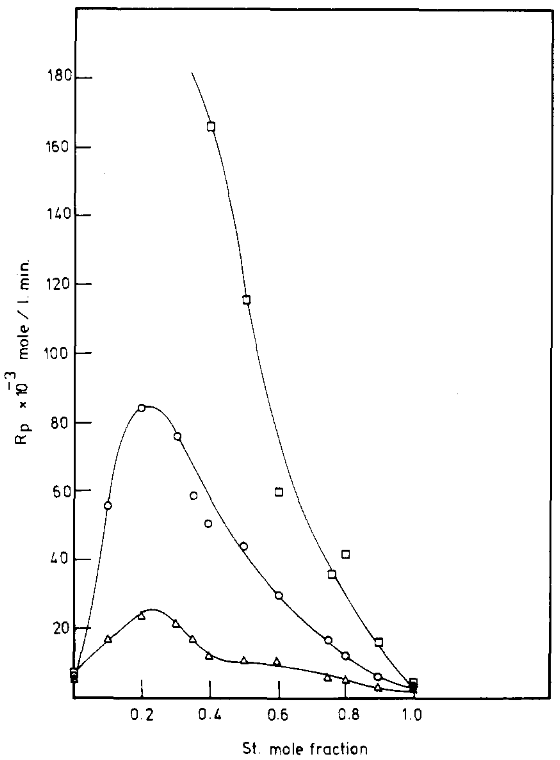

Figure 6. Dependence of R_p on monomer feed composition in dioxane at various T: (△)0.5, (○)1.0, and (□)1.5 mol L^{-1}. [AIBN] = 2.7×10^{-2} mol L^{-1}; Temperature = 60 C.

process before transfer to the thermostat.

The method to quantify the model is to analyze the overall initial copolymerization rate as a function of the total monomer concentration under each fixed monomer feed composition.

In the case of a bimolecular termination, the following equations were derived by Shirota et al.[15] to quantify the degree of participation of the free monomer and the CTC monomer in the polymerization:

$$R_p = A(X)K(k_{1c}/k_{12} + k_{2c}/k_{21}X)[M_1]^2 + A(X)[M_1] \quad (1)$$

$$R_p(f) = A(X)[M_1] \quad (2)$$

$$R_p(CT) = A(X)K(k_{1c}/k_{12} + k_{2c}/k_{21}X)[M_1]^2 \quad (3)$$

$$A(X) = 2k_{21}k_{12}R_i^{1/2}X/(k_{t11}k^2{}_{21} + 2k_{t12}k_{21}k_{12}X + k_{t22}k^2{}_{12}X^2)^{1/2} \quad (4)$$

$$R_i = 2k_d fI$$

$$[M_2] = X[M_1]$$

$$R_p/[M_1] = A(X)K(k_{1c}/k_{12} + k_{2c}/k_{21}X)[M_1] + A(X) \quad (5)$$

$$F(X) = K(k_{1c}/k_{12} + k_{2c}/k_{21}X) \quad (6)$$

Here X is the monomer feed molar ratio as represented above, K is the equilibrium constant for the formation of the CTC monomer, and k_{t11}, k_{t22}, and k_{t12} are the rate constants for the bimolecular, homo, and crosstermination reactions of growing polymer radicals, respectively. The overall initial rate R_p is the superposition of the reaction rates of the free monomer R_p(f) (eq 2) and of the CTC monomer R_p(CT) (eq 3).

The application of this kinetic scheme to the St–2CMI copolymerization has been tested. M_1 represents styrene, M_2, 2CMI; C is the complex between them.

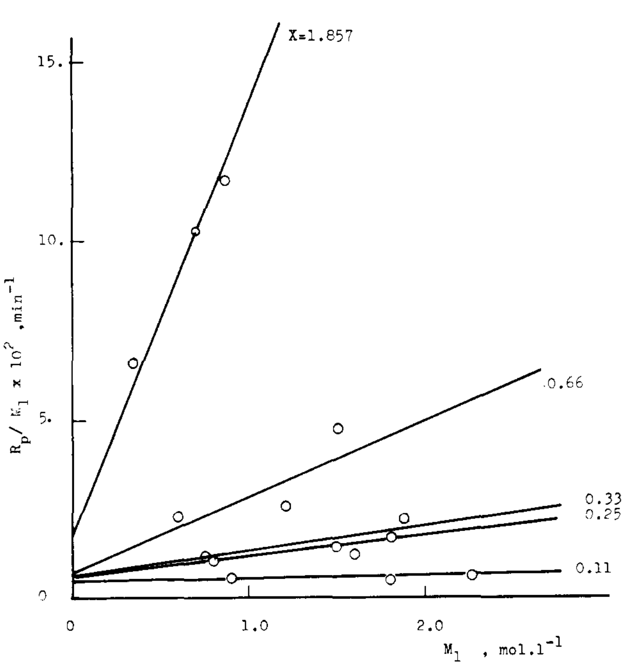

Figure 7. Dependence of the R_p/[St] on [St] at various monomer feed ratios. Solvent was chloroform.

The advantage of these equations is that one can estimate quantitatively the degree of participation of the CTC in the copolymerization process without a precise estimation of the equilibrium constant of CTC formation; its exact value is required when the individual rate constants are to be calculated.

The data in Tables II and III clearly indicate that the role of the CT increases appreciably with the maleimide content.

The plot of $R_p/[M_1]$ vs. $[M_1]$ according to eq 6 showed good linearity for each value of X (Figure 7) up to X = 0.66, i.e., at a styrene mole fraction of 0.4. At higher 2CMI content, the intercepts acquire negative values and the system cannot fit the model in both solvents anymore. This could be due to the fact that at a high 2CMI content the assumption of $k_{22} = 0$, which is among Shirota's restrictions, is no longer valid.

In the range of validity of the scheme it is possible to evaluate the degree of participation of the free monomers and the monomer complex in the copolymerization. The intercepts and the slopes of the lines in Figure 7 provide the values of $A(X)$ and $K((k_{1c}/k_{12}) + (k_{2c}/k_{21})X)$, respectively. The introduction of these values into eq 2 and 3 allows the values of R_p(f) and R_p(CT) as a function of X to be obtained (Tables II and III). The overall initial rate could be then separated into the rates of addition of the free monomer R_p(f) and the monomer complex R_p(C) for X up to 0.66. (In chloroform the model fits up to X = 1.857.)

The degree of the complex participation depends on the composition of the monomer feed as well as on the total monomer concentration.

It is possible to get a qualitative estimation of the relative reactivity between the St–2CMI complex and the free monomers toward growing polymer radicals by calculating the values of $K((k_{1c}/k_{12}) + (k_{2c}/k_{21})X)$, which has been defined by Shirota et al. as $F(X)$, from the values of $A(X)$ and $A(X)K((k_{1c}/k_{12}) + (k_{2c}/k_{21})X)$ for each value of X. The plot of $F(X)$ vs. X is presented in Figure 8 in both solvents. The values of $K(k_{1c}/k_{12})$ and $K(k_{2}c/\bar{k}_{12})$ are 0.277 and 3.67 respectively in chloroform and 0.78 and 3.986 in dioxane.

Table II
Quantitative Separation of the Overall Initial Rate of Copolymerization R_p into the Reaction Rates of the Free Monomer R_p(f) and the Charge Transfer Complex Monomer R_p(CT) as a Function of the Monomer Feed Ratios (X) at the Total Monomer Concentrations of 1.0, 2.0, and 2.5 M for the St-2CMI System in Chloroform

X	[M_1] styrene	$R_p \times 10^3$	$A(X) \times 10^3$	$A(X)K(k_{1c}/k_{12} + k_{2c}/k_{21}X) \times 10^3$	$R_p(f) \times 10^3$	$R_p(CT) \times 10^3$
0.11	0.90	4.82	4.48	0.79	4.03	0.65
	1.80	9.82			8.06	2.5
	2.25	14.79			10.00	4.00
0.25	0.80	8.00	5.28	5.21	4.22	3.32
	1.60	19.40			8.44	13.30
	2.00	33.7			10.56	20.8
0.33	0.75	8.7	5.1	7.73	3.82	4.35
	1.50	21.8			7.65	17.3
	1.875	39.4			9.50	27.2
0.66	0.60	14.0	6.27	23.32	3.76	8.35
	1.20	30.0			7.52	33.50
	1.50	71.0			9.4	52.40
1.857	0.35	22.8	18.8	127.00	6.65	15.5
	0.70	72.0			13.3	62.2
	0.875	117.0			16.6	97.23

Table III
Quantitative Separation of the Overall Initial Rate of Copolymerization R_p into the Reaction Rates of the Free Monomer R_p(f) and the Charge Transfer Complex Monomer R_p(CT) as a Function of the Monomer Feed Ratios (X) at the Total Monomer Concentrations of 0.5, 1.0, and 1.5 M for the St-2CMI System in Dioxane

X	M_1 styrene	$R_p \times 10^3$	$A(X) \times 10^3$	$A(X)K(k_{1c}/k_{12} + Xk_{2c}/k_{21}) \times 10^3$	$R_p(f) \times 10^3$	$R_p(CT) \times 10^3$
0.111	0.45	3.71	4.522	5.286	2.038	1.097
	0.90	6.8			4.069	4.28
	1.35	16.3			6.10	9.62
0.25	0.4	5.87	8.463	13.0	3.380	2.08
	0.8	14.69			6.76	8.32
	1.2	30.0			10.15	18.72
0.333	0.375	5.92	8.14	20.56	3.05	2.89
	0.76	17.78			6.10	11.56
	1.125	35.18			9.15	26.02
0.666	0.3	10	16.6	55.5	4.98	4.995
	0.6	30			9.96	19.98
	0.9	60			14.94	45.0

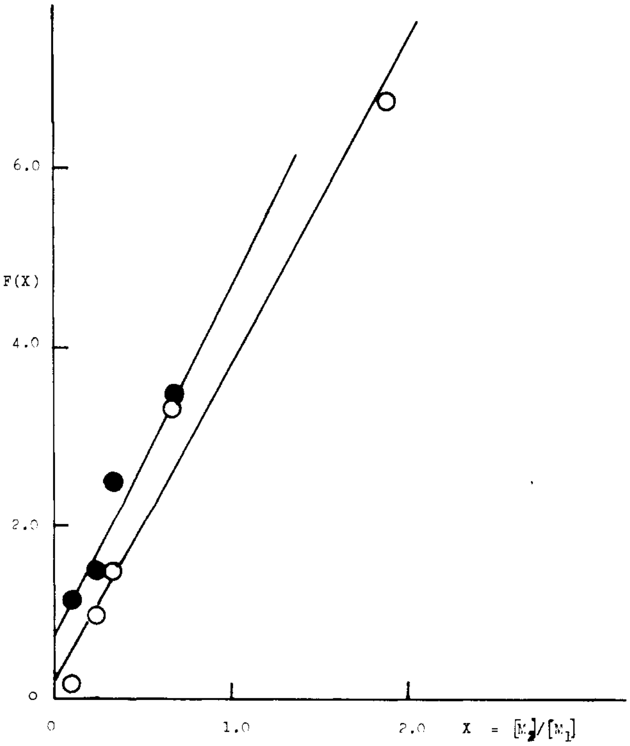

Figure 8. Plot of $F(X)$ vs. $X = [M_2]/[M_1]$ in (○) chloroform; (●) dioxane.

Considering that the value of K in dioxane is much smaller than that in chloroform, one can only conclude, at the present stage, that the complex participates appreciably in the chain propagation process and that its reactivity is higher in dioxane than in chloroform.

Registry No. 2CMI, 1203-24-3; styrene, 100-42-5.

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Acid–Base and Metal Ion Complex Formation Properties of Polymers Containing Amino Acid Residues

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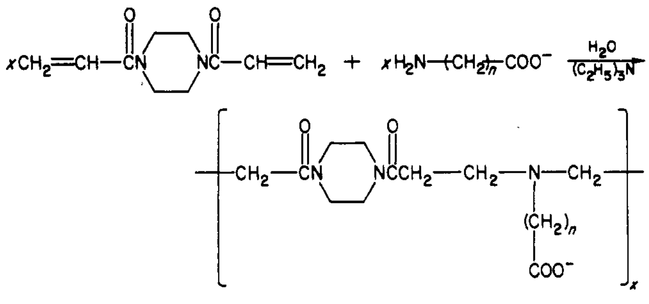
ABSTRACT: The basicity and Cu(II) ion complexation of polymers containing amino acid residues, carrying a tertiary amino group in the main chain and a carboxylic group as the side-chain substituent, have been studied in aqueous solution by potentiometric, viscosimetric, and spectrophotometric techniques. Both protonation constants of each polymer follow the modified Henderson–Hasselbach equation. The protonation of a given unit, with one exception, becomes more and more difficult as the degree of protonation of the whole macromolecule increases. A new method of computation for evaluating the stability constants of polymer–metal ion complexes from potentiometric data has been developed. The log β of the CuL^+ complex (L being the repeating unit of the polymers) decreases with increasing pH, even if the spectrophotometric parameters of the complex remain constant.

Introduction

The acid–base properties of polyelectrolytes have been extensively studied by potentiometric titration[1] and recently St. Pierre et al. proposed as a definition of the polyelectrolyte effect the difference in the apparent pK values at the extremes of the titration curve for a polyacid or polybase.[2] In other words, a polymer exhibiting a strong polyelectrolyte effect shows a large change in pK on going from the uncharged state to the charged state. On the contrary, two families of polyelectrolytes exhibit basicity constants that are independent of the overall degree of protonation of the macromolecule: poly(diazacrown ethers)[3] and poly(amido amines).[4] Both series show a bulky group in their structures (i.e., macrocycles or acryloylpiperazine ring), which shelter the positive charges on the protonated nitrogens. Also, no cooperative effects between nitrogen groups belonging to different units take place in complex formation; thus "real" stability constants could be obtained with these two series of ligands.

On the other hand, we have recently found that other amino polymers, which contain tertiary amino groups in the main chain, and are structurally related to poly(amido amines), for instance poly(β-amino sulfones)[5] and poly(β-amino ketones),[5] exhibit intermediate behavior between poly(amido amines) and "classical polyelectrolytes". As a further development of our studies on poly(amido amine) chemistry, we thought it interesting to investigate the protonation and Cu^{2+} complexation of polymeric amino acids having the structure of poly(amido amines) bearing carboxyl groups as side substituents, obtained by the polyaddition of ω-amino acids to 1,4-diacryloylpiperazine[6] according to a general synthetic route (Scheme I) for this class of polymers[7].

Scheme I



PAAA$_n$
$n = 1, 2, 4, 5$

It was immediately apparent that these new polyelectrolytes did not follow the pattern usually found in poly(amido amines), since the basicity and the complexing ability of the ionic groups of each unit did depend on the overall degree of protonation and complexation of the whole macromolecule. In order to study these polymers in solution, it was necessary to use a method of calculation different from those previously used in the case of poly(amido amines).[8] As far as protonation was concerned, a method had been already developed. However, the methods of calculation described in the literature[9] for determining the stability constants of metal ion complexes of polyelectrolytes whose repeating units do not behave independently were not entirely satisfactory, especially as a clear picture of the trend followed by these constants as a function of pH, in the case of polyelectrolytes whose basicity constants also depend on pH, was needed.

The aim of this paper is to report the synthesis of the above new family of polyampholytes, a new method of

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