Table 2 Equilibrium uptake (w/w %) and k (s^{-1}) for various NC/NG films

	10% NG		35% NG		45% NG	
Film composition	c_∞	k	c_∞	k	c_∞	k
IPN	32.3	0.0018	34.9	0.0016	41.6	0.0014
Acetone	17.9	0.0054	17.7	0.0050	19.0	0.0046

about 90%. In such treatment it is necessary to know c_∞ accurately, and this figure is more difficult to obtain with IPN than with acetone, probably because conditions are closer to saturation.

Table 2 gives the equilibrium uptake (as a percentage of the initial film weight) and k, calculated in the above manner, for a series of NC/NG films. It can be seen that whilst there is a tendency for the equilibrium uptake to increase with increasing NG content (particularly noticeable for IPN sorption), there is a corresponding fall in the value of k.

In comparing these values with those for pure NC films it must be remembered that the latter absorb by a Case II mechanism and any attempt to analyse by equation (2) will give a value of k which depends on film thickness[1]. However, for films of comparable thickness, $t_{1/2}$, the time taken for uptake to half the equilibrium value, is about 30 times greater for NC than for NC/NG films in the case of IPN and about 3 times greater than in the case of acetone. Thus plasticization by NC increases the rate of sorption, but once sufficient plasticizer is present to change the rate controlling mechanism from Case II to Case III further addition has a comparatively small effect.

A warning is frequently given that 'a moving boundary does not necessarily imply a Case II mechanism', and for Case II to be proved it is necessary to show that the boundary moves linearly with time. We would add a second warning—that a $t^{1/2}$ sorption law, particularly if approximate, does not necessarily imply Fickian diffusion. Film thickness should always be an examined parameter, and Fickian sorption is only proved if uptake is proportional to $t^{1/2}/l$.

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Reactivity ratios of styrene–*N*-iso-butylmaleimide and methyl methacrylate–*N*-iso-butylmaleimide

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The copolymerization of styrene and methyl methacrylate with *N*-isobutylmaleimide (*N*-iso-BMI) has been investigated. The reactivity ratios of these pairs of comonomers were determined by following the Fineman–Ross method. *N*-iso-BMI was found to be of limited use in modifying methylmethacrylate but was better suited to mass polymerization of styrene.

Keywords Polymerization; reactivity ratio; styrene; methyl methacrylate; *N*-isobutylmaleimide; modification

INTRODUCTION

Within the scope of our investigations concerning the chemical modification of vinyl polymers with heterocyclic monomers we have investigated the copolymerization of styrene and methyl methacrylate with *N*-iso-butylmaleimide. Because the constitution of the copolymer is a function of the reactivity ratios we have found it useful to determine these values for the copolymerization of *N*-iso-butylmaleimide with styrene and methyl methacrylate. As far as we know the reactivity ratios for the above mentioned pairs of comonomers have not yet been presented.

In determining the reactivity ratios we followed the Fineman–Ross method[1] making use of the equation

$$\frac{P-1}{R}=r_1-\frac{P}{R^2}r_2$$

where: P is the molar ratio of the comonomers in the copolymer; R is the initial ratio of molar concentrations of the comonomers; r_1 is the reactivity ratio of styrene or methyl methacrylate and r_2 is the reactivity ratio of *N*-iso-butylmaleimide.

EXPERIMENTAL

Monomers

(i) *N*-iso-butylmaleimide (N-iso-BMI) was obtained by a two stage method[2,3]. In the first stage of the reaction, from a maleic anhydride and isobutylamine in toluene at 363K we obtained *N*-iso-butylmaleamic acid which was then submitted to cyclodehydration in methylene chloride at 273K; acetic anhydride and triethylamine were used as catalysts. The product was purified by distillation under reduced pressure (30 mm Hg) at 343–348K. *N*-iso-

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Table 1 Copolymerization of styrene (M_1) with *N*-iso-Butylmaleimide (M_2). Time of copolymerization was 8–12 min. Concentration of initiator 0.1 (% by weight)

	Constitution of initial mixture of monomers		Degree of reaction			Nitrogen content (% by weight)		
	M_1	M_2	Series I	Series II	Series III	Series I	Series II	Series III
1	0.095	0.005	3.11	4.59	3.72	3.70	3.85	4.05
2	0.090	0.010	7.39	3.78	4.47	4.40	4.80	4.80
3	0.085	0.015	3.43	2.62	3.87	4.95	5.35	5.30
4	0.080	0.020	4.33	4.46	4.37	5.35	5.70	5.60
5	0.075	0.025	3.10	6.20	2.88	5.70	6.05	5.90
6	0.070	0.030	6.45	2.71	3.19	5.95	6.30	6.20
7	0.065	0.035	4.87	3.42	4.16	6.20	6.50	6.40
8	0.060	0.040	8.98	5.76	3.17	6.45	6.75	6.60
9	0.055	0.045	3.52	6.98	3.36	6.75	6.85	6.80

Table 2 Copolymerization of methyl methacrylate (M_1) with *N*-iso-Butylmaleimide (M_2). Time of copolymerization was 25–45 min. Concentration of initiator 0.1 (% by weight)

	Constitution of initial mixture of monomers		Degree of reaction			Nitrogen content (% by weight)		
	M_1	M_2	Series I	Series II	Series III	Series I	Series II	Series III
1	0.095	0.005	5.41	10.71	5.95	0.55	0.50	0.67
2	0.090	0.010	7.53	6.04	11.78	0.90	0.80	1.00
3	0.085	0.015	6.44	8.29	6.05	1.13	1.04	1.26
4	0.080	0.020	3.91	6.80	7.53	1.29	1.24	1.50
5	0.075	0.025	6.96	12.15	6.87	1.42	1.44	1.72
6	0.070	0.030	8.60	7.72	6.45	1.52	1.62	1.93
7	0.065	0.035	4.88	7.37	8.29	1.61	1.78	2.17
8	0.060	0.040	7.15	8.91	8.39	1.69	1.94	2.28
9	0.055	0.045	6.73	10.24	7.37	1.73	2.08	2.43

BMI was obtained as white needles m.pt. 319-320K.

(ii) Methyl methacrylate (from POCH Gliwice). The inhibitor was removed by washing with a 5% aqueous solution of acid sodium sulphate and an 8% aqueous solution of sodium hydroxide with distilled water. The styrene was then dried over anhydrous magnesium sulphate.

$$n_D^{20} = 1.4137$$

(iii) Styrene (from POCH Gliwice). The inhibitor was removed by washing with a 5% aqueous solution of acid sodium sulphate and an 8% aqueous solution of sodium hydroxide with distilled water. The styrene was then dried over anhydrous magnesium sulphate.

$$n_D^{20} = 1.5444$$

Reactivity ratios

The reactivity ratios were determined by the Fineman and Ross method. The copolymerizations were carried out at 348±0.5K with azobisisobutyronitrile as the catalyst. Styrene and *B*-iso-BMI were copolymerized in mass form and methyl methacrylate and *N*-iso-BMI in benzene solution. The copolymers were purified by twice precipitating from benzene solution with methanol and dried in vacuum to a constant weight. The copolymers were analyzed for nitrogen by the Kjeldahl method.

RESULTS

For the pairs of comonomers styrene –*N*-iso-BMI and methyl methacrylate —*N*-iso-BMI, three series of measurements were taken. In each of the series, nine copolymers were obtained with different precisely determined compositions (*Tables 1* and *2*). Each copolymer was analyzed for nitrogen five times. This was necessary to determine the molar ratio of comonomers in a (given) copolymer. The results obtained were plotted, the contents of nitrogen as a function of the molar share of the imide in the copolymer from which the percentage contents of nitrogen were read for particular pairs of comonomers (*Tables 1* and *2*). For each series of experiments the dependencies of $P-1/R$ on the function P/R were plotted on the basis of the reactivity constants that were determined by the least-squares method (*Table 3*).

Table 3 Copolymerization of *N*-iso-butylmaleimide with styrene and methyl methacrylate

M_1	r_1	r_2
Styrene	0.071 + 0.015	1.438 + 0.136
Methyl methacrylate	1.990 + 0.200	0.000

DISCUSSION

In the copolymerization of methyl methacrylate *N*-iso-BMI we have observed a marked decrease in the rate of reaction of copolymerization with an increase in proportion of the imide in a mixture of the comonomers. Since the concentrations of the imide in the output mixture of the comonomers is in the range 0.005-0.015 mols, it is not possible to arrive at a fully convincing geometrical interpretation. We have taken a section of the straight line corresponding to concentrations ranging from 0.015 to 0.045 mols for calculation of the reactivity ratios. The reactivity ratios determined in this way confirm our earlier observations that, in the methyl methacrylate-imide system the imide itself is more ready to copolymerize. In consequence, this leads to a considerable enrichment of the copolymer in methyl methacrylate in comparison with the initial mixture of the comonomers. If, additionally we take into consideration the low solubility of the imide in methyl methacrylate it is necessary to classify it as a factor which is of limited use in modifying methyl methacrylate. Alternatively, *N*-iso-BMI can, in a relatively broader range of concentrations, copolymerize in the mass form with styrene. The reactivity ratios observed indicate that in the copolymerization of styrene–*N*-iso-BMI the reaction of mass radicals with the imide ($r_1 < 0$, $r_2 > 0$) will be facilitated. This results in enrichment of the copolymer in *N*-iso-BMI in comparison with the initial mixture of the comonomers. If we take into consideration the fact that the presence of heterocyclic imide units in the chain of a copolymer gives the copolymer on the whole, better properties. Looking at its thermal resistance, we must estimate *N*-iso-BMI as positive modifying factor for polystyrene.

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Macroinorganics: 8.* Chelation of copper(II) ion with some new poly(amido-amines)

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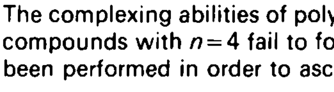
The effect on Cu(II) complexing ability of the number (n) of methylenic groups between aminic nitrogens has been studied for two classes of poly (amido-amines). In order to better elucidate the mechanism of complex formation, low molecular weight models of the polymers have also been studied. The complexing abilities of polymers and models are very similar and decrease by increasing n. Indeed compounds with $n = 4$ fail to form complexes in aqueous solution. Some viscosimetric titrations have been performed in order to ascertain possible conformational transitions upon complexation.

Keywords Complex; poly(amido-amines); chelation; copper ion; viscometric titration; nitrogen

INTRODUCTION

We have recently studied the basicity[1] and complexing ability[2] of a new class of linear amino polymers: poly(amido-amines) in aqueous solution. We recall that these polymers look like non-macromolecular bases towards protonation and complex formation allowing the determination of 'sharp' thermodynamic properties[3]. As part of a comprehensive research programme designed to give a better insight into the reasons for the unusual behaviour of poly(amido-amines) we have recently studied the effect on stepwise protonation of the length of the aliphatic chain between the amino groups present in the monomeric unit[4]. In order to better ascertain specific effects due to the macromolecularity we have also studied a set of non-macromolecular model compounds.

Pn



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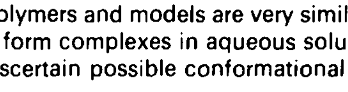

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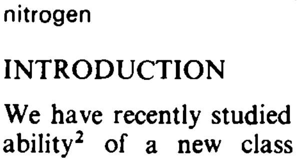

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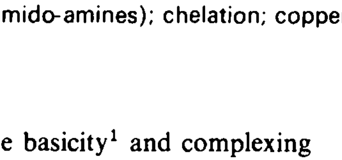

The aim of the present work is to widen the above study to the complex-formation behaviour, by reporting some results on the coordinating abilities towards copper(II) of poly(amido-amines), as a function of the length of the aliphatic chain within the monomeric units. The study has been carried out by potentiometric, spectrophotometric and viscosimetry techniques, and the conformational transitions upon complexation have been analyzed.

EXPERIMENTAL

Materials

The synthesis of polymers and the corresponding models have been previously reported[4].

CO_2-free NaOH solutions were prepared, stored and standardized as described elsewhere[5]. Stock solutions of 0.1 M NaCl were prepared from sodium chloride (C.Erba, ACS grade) without further purification and used as the ionic medium for potentiometric and viscosimetric measurements.

Emf measurements

Potentiometric titrations were carried out using a digital PHM-84 Radiometer potentiometer, an Ag–AgCl reference electrode, an Orion 91–01–00 glass electrode, and a salt bridge containing 0.1 mol dm^{-3} NaCl solution. All the titration operations (the amount of the titrant

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