Ionomers in low-polarity solvents

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A sedimentation and viscometric study was carried out with a neutralized copolymer of methacrylic acid and methyl methacrylate in tetrahydrofuran as a model ionomer in a low-polarity solvent. Viscosity measurements gave the usual result for ionomers in a low-polarity solvent. At a low concentration the reduced viscosity of the neutralized sample is lower than that of a non-neutralized one, while at a higher concentration this is the other way round. On the contrary, within the whole concentration range under study, the sedimentation coefficients of the neutralized copolymer are higher than those of the non-neutralized sample, and the plot of the reciprocal value of the sedimentation coefficient against concentration is linear in both cases as usual. The sedimentation and viscosity measurements can be made to comply, if one assumes that intermolecular association in non-polar solvents takes place already at low concentrations. Non-radiative energy transfer between donor and acceptor attached to the same ionomer molecule suggests that at a low concentration the individual ionomer molecules are contracted compared with the non-neutralized copolymer, and that, with increasing intermolecular association due to increasing concentration of the ionomer, the dimensions of the particular ionomer molecule also increase.

(Keywords: ionomers; methacrylic acid copolymers; viscosity and sedimentation behaviour; low-polarity solvents)

INTRODUCTION

Polymers containing a relatively low fraction of ionic groups are called ionomers. Although, in fact, we have here a special kind of polyelectrolyte (and in some cases they behave like other polyelectrolytes), they deserve a special name, because they possess some specific properties. For instance, if the fraction of ionic groups is sufficiently low, they may be dissolved in low-polarity solvents, such as tetrahydrofuran (THF), dioxane, or xylene[1]. If the viscosity of such a solution is compared with that of a solution of the polymer precursor, important deviations can be observed. At sufficiently low concentrations, the viscosity of the ionomer solution in low-polarity solvents is lower than that of the corresponding solution of the polymer precursor; at a certain concentration the concentration dependences of the viscosity of ionomer and precursor solutions cross each other, the viscosity of the ionomer solution goes on increasing strongly with concentration, and the solution turns into a gel. With respect to the low polarity of the solvent, one may assume that ions are present in solution as ionic pairs, among which attractive forces are operative as a result of dipole–dipole interactions. Association occurs, which is mainly intramolecular at low concentrations[2], and intermolecular at higher concentrations. It was assumed, originally, that the transition between intramolecular and intermolecular association takes place in connection with reaching the overlap concentration, near the concentration at which the viscosities of the ionomer and precursor solutions are equal. An attempt was made[3] to follow this transition by employing a technique that was used in the detection of the overlap concentration with non-ionic polymers, i.e. by non-radiative energy transfer. The attempt failed, not only due to limitations of the technique used, which formerly were not considered, but—as shown by recent results of light[4,5] and neutron[6] scattering—because intermolecular association occurs also at low concentrations.

In this study we report the results of viscosity and sedimentation measurements carried out with a model ionomer, i.e. the copolymer of methyl methacrylate (MM) and methacrylic acid (MA), in tetrahydrofuran as a low-polarity solvent. Our objective consists of obtaining information not only on intra- and intermolecular associations, but also on the size of the individual macromolecules in the aggregates. According to the extensive neutron scattering data, the size of the individual macromolecule remains unchanged with increasing aggregation, being comparable with that of the molecule of the polymer precursor[6,7]. This is also why we performed some fluorescence measurements.

EXPERIMENTAL

Polymers

The samples were prepared by radical copolymerization in bulk at 60°C with azobisisobutyronitrile (AIBN) as initiator. The degree of conversion was below 10%. Methyl methacrylate (MM) and methacrylic acid (MA) were redistilled prior to use; 2-(*N*-carbazolyl)-ethyl methacrylate (CEM) and 9-anthrylmethyl methacrylate (AMM) were prepared and kindly supplied by Dr Chalabala from IMC, Prague. The polymers thus obtained, the copolymer of MM and MA (CMMA) and the copolymer of MM, MA, AMM and CEM (CMMAdl) were precipitated into methanol and repeatedly reprecipitated from acetone into methanol. Neutralization was carried out using sodium methoxide in a dioxane/methanol mixture. To ensure solubility in THF, neutralization was conducted to two-thirds only. The polymers obtained are denoted below as CMMA-Na and CMMAdl-Na.

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Table 1 Characterization of samples. Intrinsic viscosities in 2-ethoxyethanol at 25°C are denoted as $[\eta]_{EC}$. Mole fractions of MA, AMM and CEM are denoted x_{MA}, x_{AMM} and x_{CEM}

Sample	x_{MA}	x_{AMM}	x_{CEM}	$[\eta]_{EC}$ ($cm^3 g^{-1}$)
CMMA	0.047	–	–	56.3
CMMAdl	0.046	0.0019	0.0037	58.2

Characterization of samples

The content of carboxylic groups was determined by titration with sodium methoxide in the dioxane/methanol (5/1) mixture using phenolphthalein as indicator. The content of labels was determined from absorption spectra obtained with a Perkin–Elmer 340 spectrophotometer, in agreement with other work[8]. Data for both samples are summarized in *Table 1*. The respective molar content of neutralized groups for (partly) neutralized CMMA and CMMAdl (denoted CMMA-Na and CMMAdl-Na) was 3.1% and 3.2%. The molecular weight of CMMA estimated from the intrinsic viscosity and sedimentation coefficient in tetrahydrofuran (THF) at 25°C on the basis of the Flory–Mandelkern invariant (cf. ref. 9) and using the partial specific volume for poly(methyl methacrylate) in THF[10] is about 700 000. With respect to small differences in the intrinsic viscosities for CMMA and CMMAdl in 2-ethoxyethanol at 25°C, a similar molecular weight may be assumed for CMMAdl.

Viscometry

Viscosity was measured in an Ubbelohde viscometer adapted for dilution. The flow times were recorded optoelectrically. The temperature was maintained with an accuracy of ±0.02°C.

Sedimentation analysis

The sedimentation measurements were carried out with a Beckman Spinco E ultracentrifuge provided with a schlieren optical system at 59 780 r.p.m. and 25°C. The sedimentation coefficients at the given concentration were calculated after the necessary pressure correction.

Fluorescence measurements

Fluorescence measurements were performed at 25°C using a home-made fluorimeter reported elsewhere[11]. Excitation was brought about by using light having wavelength 296 nm; non-radiative energy transfer was characterized by the light intensity ratio at 413 and 347 nm.

RESULTS AND DISCUSSION

The existing views regarding the behaviour of ionomers in low-polarity solvents are predominantly based on viscosity measurements. This is why basic measurements carried out by us concerned the concentration dependences of reduced viscosity for the non-neutralized (CMMA) and neutralized (CMMA-Na) copolymer of methyl methacrylate (MM) and methacrylic acid (MA) in tetrahydrofuran (THF). The results shown in *Figure 1* are as expected. At low concentration the reduced viscosity η_{red} for CMMA-Na is lower than that for CMMA. However, in the concentration range 0.015–0.02 g cm^{-3} the reduced viscosity η_{red} of CMMA-Na increases steeply, while η_{red} of CMMA is a linear function of concentration c within the whole measured range, in agreement with the Huggins equation:

$$\eta_{red} = [\eta] + k_H[\eta]^2 c \qquad (1)$$

where $[\eta]$ is the intrinsic viscosity and k_H is the Huggins coefficient. For the sake of comparison, *Figure 1* also shows data for CMMA in 2-ethoxyethanol (EC), which for copolymers of MM with a low quantity of MA is a poor, almost theta, solvent[12].

Results of the sedimentation analysis offer a quite different picture, however. *Figure 2* shows the dependence of the reciprocal value of the sedimentation coefficient s on concentration. Within the concentration range under

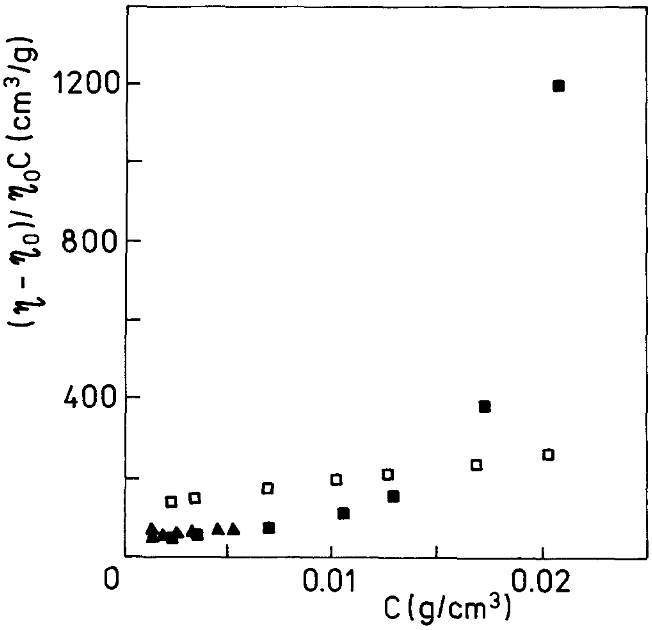

Figure 1 Dependence of reduced viscosity on concentration for the neutralized and non-neutralized copolymer at 25°C: (□) CMMA, THF; (■) CMMA-Na, THF; (▲) CMMA, EC

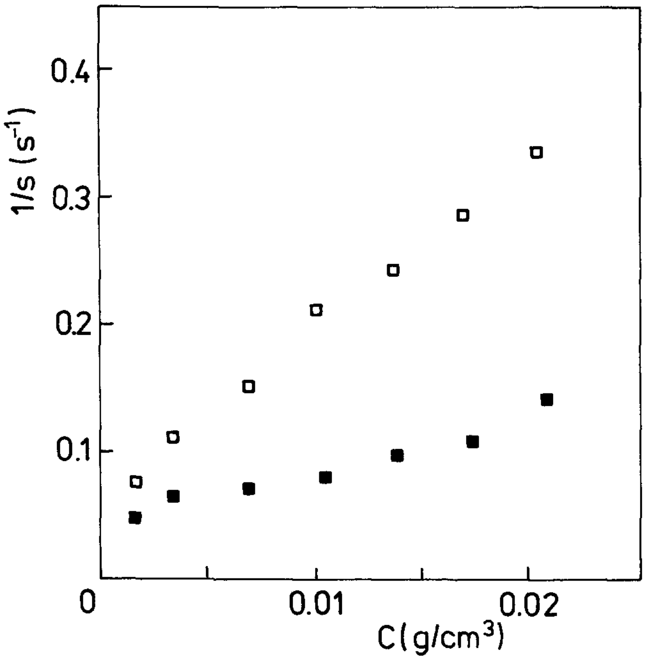

Figure 2 Concentration dependence of the sedimentation coefficient at 25°C: (□) CMMA; (■) CMMA-Na

investigation, there is no concentration at which the sedimentation coefficient s would have the same value for CMMA and CMMA-Na: the value of s for CMMA-Na is higher throughout the whole range. Both plotted dependences are linear as usual, i.e. for the sedimentation coefficient we have:

$$s = s_0/(1 + k_s c) \qquad (2)$$

where $s_0 \equiv \lim_{c \to 0} s$ and k_s is the coefficient of the concentration dependence of the sedimentation coefficient.

The first conclusion that may be drawn is that, at the concentration c_η for which η_{red} for CMMA and CMMA-Na are the same, CMMA-Na does not assume hydrodynamic properties identical with those of CMMA. In the first approximation both viscosity and sedimentation coefficient are determined primarily by the size and molecular weight of particles present in solution. In this approximation we have:

$$[\eta] \equiv \lim_{c \to 0} \eta_{\text{red}} \sim R_g^3/M \qquad (3)$$

$$s_0 \sim M/R_g \qquad (4)$$

where R_g is the mean-square radius of gyration and M is the molecular weight. According to scattering experiments[4–7], intermolecular association of ionic pairs occurs already at very low concentrations, and the average size and average molecular weight of ionomeric particles increase with ionomer concentration. It may be assumed, therefore, that at c_η both the average size and average molecular weight of particles in CMMA and CMMA-Na solutions differ from each other, but that the effect of these differences on viscosity is compensated.

The manner in which the size and molecular weight of particles arising by the association of ionomeric macromolecules are related to each other can be deduced from the fact that also for CMMA-Na the concentration dependence of s is described in terms of equation (2). If we rule out the unlikely case that the size and molecular weight of the particles, on the one hand, and the coefficient k_s, on the other, vary simultaneously so that their mutual effect is compensated for, then—bearing in mind equation (4)—the relation $R_g \sim M$ is valid. This is also suggested by the fact that, according to sedimentation diagrams, the peaks of CMMA-Na are broader than those of CMMA but at no concentration do they show a bimodal distribution of particles (*Figure 3*). One may object that equation (4) simplifies the matter too much. However, results of neutron scattering from solutions of neutralized and partly sulphonated polystyrene[6] in THF lead to a similar conclusion, yielding $R_g \sim M^{0.94}$. Also, in a recent study involving the same type of ionomer in xylene, combined data on the dynamic and static light scattering showed proportionality between R_g and the number of mutually associated molecules[13].

Along with information regarding the size and molecular weight of particles in a low-polarity ionomer solution, neutron scattering provided[6,7] information about these quantities for an individual macromolecule included in such an aggregate. Up to now, however, we have not been able to render consistent the facts that the exponent in the relation $R_g \sim M^a$ for aggregates approaches unity and that, according to neutron scattering, the size of a particular macromolecule does not vary with the degree of aggregation. Also, in keeping with neutron scattering these sizes should correspond to those of the polymer precursor. Our results suggest something else, however. By excluding the dimensions from equations (3) and (4) we obtain $M \sim ([\eta]s_0^3)^{1/2}$. The ratio of the $([\eta]s_0^3)^{1/2}$ values for CMMA and CMMA-Na obtained by extrapolation to zero concentration in *Figures 1* and *2* is 1.03, and hence, in the limit of infinite dilution, association is virtually only intramolecular. However, since $[\eta]$ for CMMA-Na is much smaller than that for CMMA, it must be assumed that the intramolecular association leads to contraction of the ionomer molecule. In some studies[4,5] the molecular weight obtained for the ionomer in solution by light scattering amounted—even at very low concentrations—to about twice that obtained for the polymer precursor. One of the reasons for the differences may be the fact that, after the ionomer has been dissolved in the low-polarity solvent, establishment of equilibrium can take up to several days[14], which may have affected the light scattering results.

To obtain more information regarding the size of the individual ionomer molecules in the low-polarity solvent, we carried out fluorescence measurements of non-radiative energy transfer (NET), which takes place between two groups if the emission spectrum of one chromophore (donor) overlaps the excitation spectrum of the other chromophore (acceptor) and the donor is irradiated with light of a suitable excitation wavelength. The efficiency of NET, E, is strongly dependent on the distance r between donor and acceptor and is described by the relation[15]:

$$E = R^6/(R^6 + r^6) \qquad (5)$$

where R is the characteristic distance in which one-half of the energy has been transferred by NET.

For this purpose we prepared a copolymer of MM and MA labelled with carbazole and anthracene groups, which is denoted below as CMMAdl; its characteristics are summarized in *Table 1*. As the measure of NET we

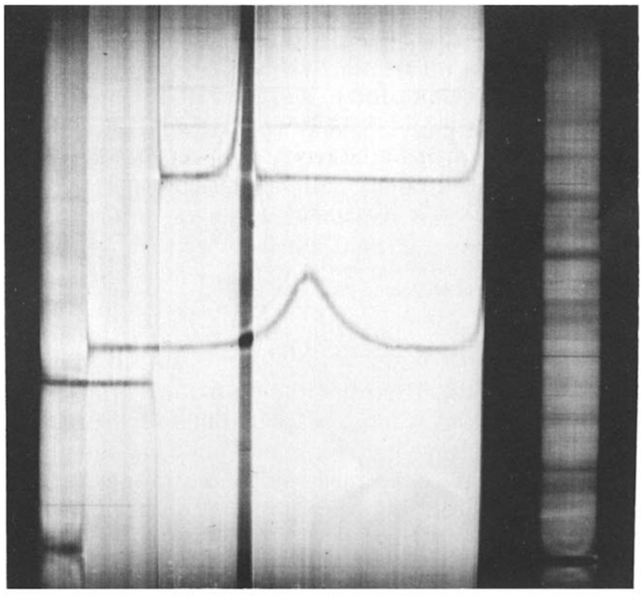

Figure 3 Sedimentation diagram in the 39th minute of the sedimentation experiment at 59780 r.p.m. and 25°C; upper curve, CMMA; lower curve, CMMA-Na. Concentration of both samples was 0.010 g cm^{-3}. The line passing through the peak for CMMA is an optical effect due to the relatively high polymer concentration and the sharpness of the peak

Table 2 Results of fluorescence measurements. Intensity ratio I_{413}/I_{347} characterizes the effectiveness of NET. Solvents: EC, 2-ethoxyethanol; THF, tetrahydrofuran; 25°C

Solvent	Concentration ($g cm^{-3}$) CMMAdl	CMMAdl-Na	CMMA-Na	I_{413}/I_{347}	η_{red} ($cm^3 g^{-1}$)
EC	0.0025	–	–	0.12	62
THF	0.0025	–	–	0.04	139
THF	–	0.0025	–	0.23	59
THF	–	0.0025	0.0200	0.04	high

chose the ratio of the intensity of light emitted at 413 nm, i.e. at the wavelength that corresponds to the maximum of the intensity of light emitted by the anthracene group (acceptor), to that at 347 nm, emitted by the carbazole groups (donor). A series of experiments summarized in *Table 2* were carried out. First, it was checked whether NET is able to detect a change in the size of the CMMAdl molecule to an extent suited for our purposes. *Figure 1* shows that the decrease in η_{red} of CMMA due to neutralization roughly corresponds to the exchange of THF, i.e. of a good solvent, for EC, i.e. a poor solvent. The emission spectrum of CMMAdl in THF contains only a single broad peak; in other words, no NET takes place here. On the other hand, the spectrum in EC contains peaks that correspond to the emission of AMM and are small but quite distinct, which means that NET is operative in this case. The emission spectrum of (partly) neutralized CMMAdl (CMMAdl-Na) in THF (at the concentration 2.5×10^{-3} g cm^{-3}) is similar to that in EC, which confirms the results of our hydrodynamic measurements, namely, that the intramolecular association reduces the size of the ionomer. The finding that the effectiveness of NET for CMMAdl-Na in THF is higher than that for CMMA in EC, in spite of η_{red} being comparable, may be attributed to the association of CMMAdl-Na molecules, which raises both η_{red} and the efficiency of NET.

Another matter to be checked was the question whether the size of a particular macromolecule varies with increasing intermolecular association. We therefore prepared a solution containing 0.0025 g cm^{-3} CMMAdl-Na and 0.02 g cm^{-3} CMMA-Na. Similarly to CMMAdl in THF, according to the recorded spectrum there is no NET in this case either. This finding indicates that the size of the molecule has increased.

CONCLUSIONS

The viscosity, sedimentation and fluorescence measurements reported in this study offer a consistent view regarding the behaviour of ionomers in low-polarity solvents. In the limiting case of infinite dilution, if the solution is in equilibrium, only intramolecular associations are operative, leading to contraction of the macromolecule. At finite concentrations the existence of intermolecular association, which leads to the formation of aggregates, should be considered from the very beginning. The fraction of intermolecular interactions increases with concentration. The sizes of the aggregates expressed through the mean-square radius of gyration are roughly proportional to their molecular weight. The size of a particular molecule included in the aggregate increases with the degree of aggregation. If there is any sense in talking about the overlap concentration, the latter cannot be connected with a sudden transition from intramolecular to intermolecular association, because such a change takes place starting from the lowest concentration.

It seems clear that intermolecular association starts to become operative together with intramolecular association already at low concentrations. However, there is a contradiction regarding the size of the associated particular macromolecule. In this respect our conclusions deviate from the results of neutron scattering[6,7]. Elucidation of this contradiction calls for further theoretical and experimental work. It should be pointed out that our results are only qualitative in this respect, but that, on the other hand, the results of neutron scattering are not quite unambiguous either[16].

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