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PII: S0032-3861(97)00490-4

Polymer Vol. 39 Nos. 8–9, pp. 1749–1751, 1998

0032-3861/97/$17.00+0.00

polymer communications

Poly(*N*-isopropylacrylamide-*co*-acrylic acid) ionomers with a controllable molar mass and ionic content

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(Revised June 1997)

The preparation of poly(*N*-isopropylacrylamide-*co*-acrylic acid) ionomers with different desirable molar masses and ionic contents has accomplished by using a benzene/ethanol mixture as polymerisation medium, wherein benzene and ethanol acted as solvent and chain transfer agent, respectively. The volume ratio of benzene to ethanol in the mixture could be used to control the molar mass of the ionomer in a broad range from $\sim 10^4$ to $\sim 5 \times 10^6$ g mol^{-1}. The ionic content was less affected by the solvent composition, but regulated by the monomer feed ratio. The ionomers were characterised by a combination of static and dynamic laser light scattering. The molar mass distributions of the ionomers were much narrower than those expected from free-radical polymerisation. The light scattering results revealed that the translational diffusion coefficient (D) scaled to the molar mass (M) as D (cm^2 s^{-1}) $= 3.56 \times 10^{-4} M^{-0.61}$. © Elsevier Science Ltd. © 1997 Elsevier Science Ltd. All rights reserved.

(**Keywords:** *N*-isopropylacrylamide; ionomer; laser light scattering)

Introduction

Poly(*N*-isopropylacrylamide) (PNIPAM) is a well known water soluble thermal sensitive polymer[1,2]. It exhibits a lower critical solution temperature (LCST) at ~32°C. Due to its easily accessible critical temperature, the phase behaviour of PNIPAM is of a special interest to many researchers. As a good model system, PNIPAM has been used to study the coil-to-globule transition[3,4]. As a promising material, PNIPAM and its derivatives have demonstrated a wide range of applications in biotechnology, drug controlled release, flocculation and water treatment[5–11].

Introducing a few percent of ionic groups into PNIPAM through a free radical copolymerisation is a common method to get PNIPAM derivatives with different properties. By varying the type and content of ionic groups, we can manipulate the properties of PNIPAM for a specific application. For example, the thermal sensitive flocculants patented by Guillet *et al.*[7] are actually anionic or cationic PNIPAM ionomers. The PNIPAM ionomers normally have a higher LCST than the PNIPAM homopolymer and the LCST increases as the content of ionic groups increases.

In spite of extensive interest in PNIPAM ionomers, few fundamental studies have been reported[12]. Deng and Pelton[13] found that a cationic PNIPAM ionomer, poly(*N*-isopropylacrylamide-*co*-diallyldimethylammonium chloride) (PNIPAM-*co*-DADMAC), was able to form a stable colloid even at temperatures much higher than its phase separation temperature because of the electrostatic repulsion between the cationic DADMAC groups on different colloidal particles. The particle size was varied in the range of 50–250 nm, depending on the ionic content, temperature, pH and the salt concentration. However, due to the low reactivity of DADMAC, the highest content of DADMAC in the ionomer was ~2 mol%, which limits the study of the PNIPAM/DADMAC ionomers within a very small window of the ionic content.

Note that a set of PNIPAM ionomers with a controlled molar mass and charge density are essential toward better understanding of the colloidal behaviour of PNIPAM ionomers in aqueous solution, we have developed a synthetical method to prepare anionic poly(*N*-isopropylacrylamide-*co*-acrylic acid) (PNIPAM/AA) ionomers with a well-defined molar mass and ionic content by simply varying the composition of the copolymerisation medium, a mixture of benzene and ethanol. Details of the preparation and characterisation of the ionomers are reported as follows.

Experimental

Materials. *N*-isopropylacrylamide (NIPAM, courtesy of Kohjin Co., Japan) was purified by recrystallisation in a benzene/*n*-hexane mixture. Acrylic acid (AA) was distilled under reduced pressure at 40°C to remove the inhibitant. Azobisisobutyronitrile (AIBN) was recrystallised in methanol. All the solvents used were analytical grade and freshly distilled.

Synthesis. The ionomer samples were prepared by free-radical polymerisation in benzene, ethanol or a benzene/ethanol mixture at 60°C using AIBN as initiator. The reaction was conducted in a 250-mL two-neck flask equipped with a nitrogen inlet tube and a magnetic stirrer. 0.5 mmol of NIPAM, proper amount of AA and 0.5 mol% of AIBN were added to 50 mL of the solvent. The total monomer concentration was kept close to 0.5 M. After a 30-min nitrogen purging, the reaction mixture was heated to 60°C and the reaction was carried out at this temperature for 1 h in an oil both. The monomer conversion was controlled to be less than 50%. After the termination of the reaction, the solvent was evaporated at $T < 40$°C by a reduced-pressure distillation. Each product of the ionomer was purified through three cycles of the acetone-to-hexane reprecipitation[14].

The selection of such a solvent mixture was based on the following consideration. It is known that in the preparation of PNIPAM homopolymer, using benzene as solvent can yield higher molar mass samples than using other solvents.

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On the other hand, it is also known that alcohol is a relatively moderate chain transfer agent for free radical polymerisation[15]. Therefore, it is possible to control the molar mass by using a benzene/ethanol mixture with a varied composition[16].

The ionic content of each ionomer was determined by titration using a 0.01 M potassium hydroxide solution with phenolphthalein as indicator. A distinct colour change from colourless to red was used as an indication of the end point. Thereafter, the copolymer of NIPAM and AA in acid form is denoted as PNIPAM–mAA, where m represents the mole content of AA in the copolymer. The molar mass distributions of the copolymers were characterised by a combination of static and dynamic laser light scattering.

Laser light scattering. A commercial LLS spectrometer (ALV/SP-125) with an ALV-5000 digital time correlator and a solid-state laser (ADLAS DPY425II, output power ~400 mW at $\lambda = 532$ nm) as light source was used. The incident light beam is vertically polarised with respect to the scattering plane. The static LLS measurements were carried in the angular range 20–150°. The angular dependence of the excess absolute time-averaged scattering intensity, known as Rayleigh ratio $R_{vv}(q)$, is measured. For a dilute solution, we have:

$$\frac{KC}{R_{vv}(q)} \approx \frac{1}{M_w}\left(1+\frac{1}{3}R_g^2q^2\right)+2A_2C \qquad (1)$$

where $K = 4\pi n^2(\mathrm{d}n/\mathrm{d}C)^2/(N_A\lambda_0^4)$ with N_A, n and λ_0 being Avogadro's constant, the solvent refractive index, and the wavelength of light in a vacuum, respectively; $q = (4\pi n/\lambda_0)\sin(\theta/2)$ with θ being the scattering angle. It should be noted that the AA content of the copolymer is only ~6% and the specific refractive index increment of AA is close to that of PNIPAM (0.107 mL g^{-1}). Therefore, we can ignore the composition effect and treat these copolymers as PNIPAM homopolymers since no more than 1% error will be introduced, which is much smaller than the intrinsic error of a light scattering experiment. By measuring $R_{vv}(q)$ at a set of C and θ, we were able to determine the weight-average molar mass M_w, and the radius of gyration $\langle R_g^2\rangle^{1/2}$ (or $\langle R_g\rangle$), the second virial coefficient A_2 on the basis of equation (1).

In dynamic LLS, the measured intensity–intensity time correlation function $G^{(2)}(t,q)$ in the self-beating mode was analysed by the Laplace inversion program (CONTIN) in the correlator, resulting in a corresponding line width distribution $G(\Gamma)$[17]. All the dynamic LLS experiments were made at a low scattering angle of $\theta = 15°$, which has ensured that $q\langle R_g\rangle < 1$, so that the extrapolation of $(\Gamma/q^2)_{q\to 0}$ is not necessary. For a diffusive relaxation, $G(\Gamma)$ can be reduced to a translational diffusive coefficient distribution $G(D)$ and further to a hydrodynamic radius distribution $f(R_h)$ on the basis of $D = k_BT/6\pi\eta R_h$, where k_B, T, and η are the Boltzmann constant, the absolute temperature, and the solvent viscosity, respectively.

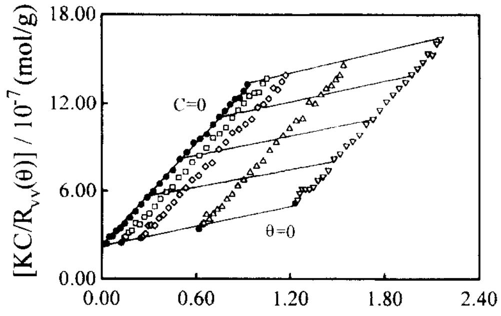

Figure 1 Typical Zimm plot of PNIPAM–0.8AA in THF at 25°C, where the concentration ranges from 5×10^{-5} to 5×10^{-4} g mL^{-1}

Results and discussion

Figure 1 shows a typical Zimm plot of PNIPAM–0.8AA in THF at 25°C. As expected, no ionic effect of the ionomer was observed in THF and the Zimm plot looks fairly normal. On the basis of equation (1), we were able to obtain M_w, $\langle R_g\rangle$ and A_2 from the extrapolations of $[KC/R_{vv}(\theta)]_{\theta\to 0, C\to 0}$, $[KC/R_{vv}(\theta)]_{\theta\to 0}$ *versus* C, and $[KC/R_{vv}(\theta)]_{C\to 0}$ *versus* q^2, respectively. All the LLS results are summarised in *Table 1*.

Table 1 clearly shows that M_w decreases as the ethanol content in the solvent mixture increases, but the ionic content has much less effect on M_w. This fact provides us with an opportunity to make a series of samples with similar average molar mass, but quite different ionic contents. The ionic content of the final copolymers is close to, or slightly higher than that in feed, indicating that the monomers AA and NIPAM have a similar reactivity in the benzene/ethanol mixture. This is quite plausible because the possible composition drift during the polymerisation has been avoided, resulting in various copolymers, each with desired molar mass and composition.

Figure 2 shows five translational diffusion coefficient distributions of the ionomer samples with different average molar masses. The average translational diffusion coefficient $\langle D\rangle$ defined as $\int_0^\infty G(D)D\mathrm{d}D$ can be obtained from $G(D)$. Furthermore, $\langle D\rangle$ can be related to the average hydrodynamic radius $\langle R_h\rangle$ by the Stokes–Einstein equation.

Table 1 Summary of reaction conditions, ionic contents, and LLS results of poly(NIPAM-*co*-AA) copolymers in THF at 25°C

Sample	Ethanol (%)	AA (mol%) In feed	AA (mol%) In polymer	M_w (g mol^{-1})	$\langle R_g\rangle$ (nm)	$\langle R_g\rangle/\langle R_h\rangle$	$\langle D\rangle$ ($\mathrm{cm}^2\,\mathrm{s}^{-1}$)	$\mu_2/\langle D\rangle^2$	M_w/M_n	M_z/M_w
NIPAM–0.8AA	0	1.0	0.8	4.7×10^6	121	1.52	3.1×10^{-8}	0.18	1.62	1.68
NIPAM–4.5AA	0	4.0	4.5	2.5×10^6	102	1.43	3.4×10^{-8}	0.21	1.73	1.86
NIPAM–2.1AA	1	2.0	2.1	5.9×10^5	64.1	1.50	5.8×10^{-8}	0.18	1.64	1.74
NIPAM–0.5AA	5	0.5	0.5	2.2×10^5	27.2	1.51	1.4×10^{-7}	0.20	1.75	1.80
NIPAM–1.1AA	20	1.0	1.1	7.4×10^4	11.4	1.50	3.2×10^{-7}	0.24	1.66	1.92
NIPAM–2.0AA	20	2.0	2.0	8.9×10^4	13.7	1.52	2.7×10^{-7}	0.22	1.74	2.02
NIPAM–4.0AA	20	4.0	4.0	6.8×10^4	10.8	1.50	3.4×10^{-7}	0.21	1.72	1.86
NIPAM–6.2AA	20	6.0	6.2	8.3×10^4	13.3	1.53	2.8×10^{-7}	0.23	1.70	1.78
NIPAM–3.3AA	100	3.0	3.3	1.2×10^4	–	–	–	–	–	–
NIPAM–4.6AA	100	4.0	4.6	1.1×10^4	–	–	–	–	–	–

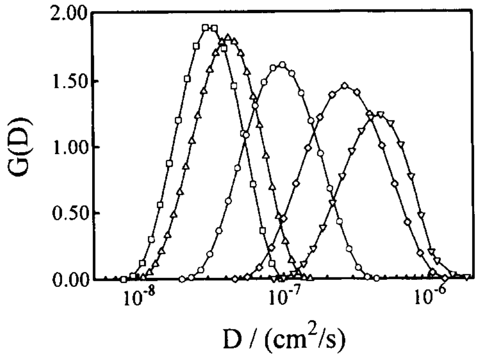

Figure 2 Translational diffusion coefficient distributions $G(D)$ of five PNIPAM–AA ionomers in THF at 25°C. □, PNIPAM-0.8AA; △, PNIPAM-4.5AA; ○, PNIPAM-2.1AA; ◇, PNIPAM-0.5AA; ▽, PNIPAM-1.1AA

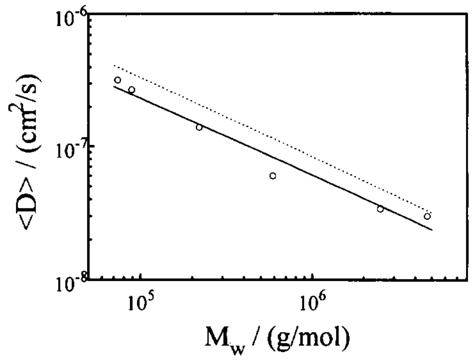

Figure 3 Double logarithmic plot of $\langle D\rangle$ *versus* M_w for PNIPAM–AA ionomers in THF at 25°C, where the solid line represents a least-squares fitting of $\langle D\rangle = 1.86 \times 10^{-4} M_w^{-0.58}$ **and the dashed line represents a calibration of** $D = 3.56 \times 10^{-4} M^{-0.61}$ for monodisperse ionomer chains

The values of $\langle D\rangle$ and $\langle R_g\rangle/\langle R_h\rangle$ are also listed in *Table 1*. The ratio of $\langle R_g\rangle/\langle R_h\rangle \sim 1.5$ shows that the ionomer chains in THF at 25°C have a coil conformation. For a linear polymer in good solvent with $\mu_2/\langle D\rangle^2 < 0.25$[18], the relative width $\mu^2/\langle D\rangle^2$ of $G(D)$ can be used to estimate the polydispersity index M_z/M_w on the basis of $M_z/M_w = 1 + 4\mu_2/\langle D\rangle^2$, where $\mu^2 = \int_0^\infty G(D)(D - \langle D\rangle)^2 \mathrm{d}D$[19]. It can be found that the M_z/M_w of these ionomers is ~ 1.8. The values of $\mu_2/\langle D\rangle^2$ indicate that the molar mass distributions are relatively narrow for polymers made via free radical polymerisation, which may be attributed to a possible fractionation introduced in the process of the sample purification.

Figure 3 shows a double-logarithmic plot of $\langle D\rangle$ *versus* M_w for the ionomers in THF at 25°C, where the solid line represents a least-squares fitting of $\langle D\rangle = 1.86 \times 10^{-4} M_w^{-0.58}$. The exponent ($-0.58$) further indicates that the ionomer chains in THF behave like typical random coils in a good solvent. A combination of M_w and $G(D)$ can lead to a calibration between D and M for monodisperse ionomer chains[20], namely, $D = 3.56 \times 10^{-4} M^{-0.61}$, which is represented by the dashed line in *Figure 3* for comparison. Using this calibration, we converted each $G(D)$ to a corresponding molar mass distribution. *Figure 4* shows five differential weight distributions $f_w(M)$ calculated from the corresponding $G(D)$ values in *Figure 2*. The polydispersity index M_w/M_n calculated from each $f_w(M)$ is also listed in *Table 1*[20], which reasonably agrees with those estimated from $\mu_2/\langle D\rangle^2$.

In conclusion, the PNIPAM–AA ionomers with a well-defined molar mass in the range of $\sim 10^{-4}$ to $\sim 5 \times 10^6$ g mol^{-1} can be prepared by a simple variation of the composition of the solvent mixture of ethanol and benzene. The degree of ionisation can be designed by the monomer ratio of NIPAM to AA in feed. The reactivities of NIPAM and AA in the mixture are similar so the ionic content in the ionomer is less influenced by the solvent composition. This leads to a way to prepare a set of the ionomers with a similar ionic content, but different molar masses, for further studies of the molar mass dependence of the PNIPAM ionomers in aqueous solution.

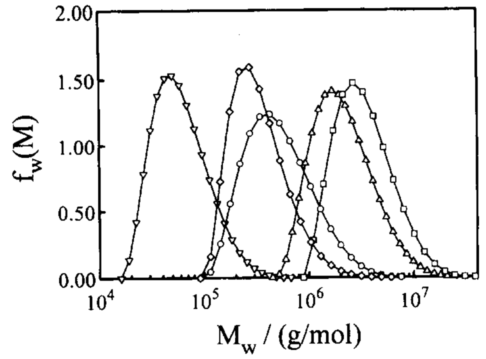

Figure 4 Differential weight distributions ($f_w(M)$) of five PNIPAM–AA ionomers: □, PNIPAM-0.8AA; △, PNIPAM-4.5AA; ○, PNIPAM-2.1AA; ◇, PNIPAM-0.5AA; ▽, PNIPAM-1.1AA

Acknowledgements

The financial support of the Research Grants Council of Hong Kong Government Earmarked Grant 1995/96 (CUHK 305/96P, 2160063) is gratefully acknowledged. Qiu is grateful to the Chinese University of Hong Kong for awarding him a one-year postdoctoral fellowship.

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