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Journal of Non-Crystalline Solids 235–237 (1998) 652–657

JOURNAL OF
NON-CRYSTALLINE SOLIDS

Light scattering investigation of self-release polymeric derivatives

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Abstract

We describe the dynamics of new slow release formulations of plant growth regulators (PGR) in aqueous solution. The new PGR formulations are water-soluble copolymers derived from acrylamide and vinyl chloroethyl ether, containing side linkages of 1-naphthylacetic acid (NAA) and 3-indolbutyric acid (IBA). In discussing the results of the light scattering experiments we are interested primarily in the varying degree of the aromatic character of the side groups. The PGR system containing NAA hydrophobic side groups leads to the formation of interpolymeric micellar structures. The hydrodynamic radius, R_h , of the parent polymer, almost doubles by incorporating the NAA linkages, but it remains approximately the same when the NAA linkages are replaced by IBA side groups of less aromaticity. The scattering intensities and apparent hydrodynamic radii display a systematic decrease as a function of time due to the loss of the IBA linkages in alkaline conditions. © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

Recently, increasing attention has been focused on various materials which are able to release a bioactive compound at controlled rates [1–4]. The latter is dependent mainly on the properties of the system and in particular, the structures of the components. Although the lower molecular weight (LMW) plant growth regulators (PGRs) have gained practical relevance, their more widespread use has been limited by a number of factors [5,6]. One of the biological shortcomings of the

LMW plant stimulants is the concentration range in which these compounds are effective. The response has an increase, then a decrease in biological activity, and moving on to a negative response with a further increase in the dose of the hormone [7,8]. New, more effective and less toxic PGRs involve modification of the LMW bioactive compounds into a controlled release form [7,9,10] that offers reduced losses and improved efficiency, greater safety towards non-target organisms, and safety to those handling the products. Moreover, the modified PGRs have a wider range of effective concentrations [11,12].

The polymeric formulations of PGRs are high molecular weight systems in which the bioactive compound PGR unit is attached to the polymeric chain by a hydrolysable chemical bond [5,7]. In

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the present work, static and dynamic light scattering data from a series of polymeric derivatives of 1-naphthylacetic acid (NAA) and 3-indolbutyric acid (IBA) are reported as a function of concentration. The light scattering data show changes and trends in the dynamics and scattering intensities. These are discussed in terms of the NAA and IBA concentration value in the polymeric form and as a function of concentration in the polymeric water solution and also as a function of time.

2. Experimental

2.1. Preparation of the polymeric NAA derivatives

Esters of NAA with the copolymer of vinyl chloroethyl ether and acrylamide were synthesized by the reaction of the NAA or IBA potassium salt with the copolymer solution in DMSO at 100°C for 8 h and by altering the reagent proportions [13,14]. The content of NAA and IBA in the polymeric esters was determined spectrophotometrically (see Table 1).

2.2. Dynamic light scattering

The experimental autocorrelation function was measured with an apparatus equipped with an argon ion laser (Coherent Radiation Model Innova 304) operating at a wavelength of 488 nm. A multibit, multi- τ full digital correlator (ALV-5000) was used that covered a dynamic range of about 10 decades.

2.3. Data analysis

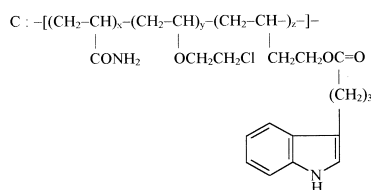
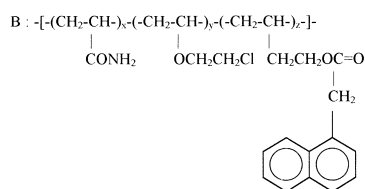
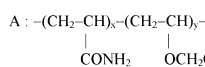
The dynamic light scattering experimental correlation functions were treated in the homodyne limit. The measured intensity autocorrelation function, $G(q,t)$, is related to the desired normalized field correlation function, $g(q,t)$, where $q = (4\pi n/\lambda)\sin(\theta/2)$ is the scattering vector, n is the refractive index of the bulk polymer, θ is the scattering angle and λ the laser wavelength by

$$G(q,t) = A \left[1 + f |ag(q,t)|^2 \right], \quad (1)$$

Table 1

Type A is the copolymer of acrylamide with vinyl chloroethyl ether with $x=92$ mol% and $y=8$ mol%. Type B is the copolymer of acrylamide with vinyl chloroethyl ether and vinyl 1-naphthylacetic acid ether with $z=1.94$ and 3.54 mol% ($x=92$ mol% and $y+z=8$ mol%). Type C is the copolymer of acrylamide with vinyl chloroethyl ether and vinyl 3-indolbutyric acid ether with $z=0.9, 3.16$ and 5.9 mol% ($x=92$ mol% and $y+z=8$ mol%).

Polymeric form	\bar{M}_w	Type of molecular structure	IBA linkage content (mol%)
PF1	18 000	A	0
PF2	19 000	B	1.94
PF3	21 000	B	3.54
PIBA1	19 000	C	0.9
PIBA2	22 000	C	3.16
PIBA3	24 000	C	5.9



where f is an instrumental factor, calculated by means of a standard, a is the fraction of the total scattered intensity associated with density fluctuations with correlation times longer than 10^{-6} s and A is the baseline. First, we fitted the $g(q,t)$ correlation functions using a sum of two Kohlrausch–Williams–Watts (KWW) functions,

$$ag(q,t) = A_f \exp \left[- (t/\tau_f)^{\beta_f} \right] + A_s \exp \left[- (t/\tau_s)^{\beta_s} \right] \quad (2)$$

with parameters $\{A_f, \tau_f$ and $\beta_f\}$ and $\{A_s, \tau_s$ and $\beta_s\}$ that give the contrast, relaxation time and shape of the fast and slow processes, respectively. Typical polarized intensity–intensity correlation functions,

$g^{(2)}(t)$, for a scattering angle of 90° are shown in Fig. 1 for the parent polymer (PF1) in pH=9 and for the NAA polymeric ester with 3.54% mol content (PF3) in pH=9. Relaxation time distributions using the inverse Laplace transform (ILT) of the time correlation functions with the REPES algorithm [15] are given in the form of $\tau A(\tau)$ versus $\log \tau$ plots and displayed in the inset of Fig. 1. The ILT result shows a double peak structure.

3. Results

The results of the fitting of the experimental correlation functions to the Kohlrausch–Williams–Watts (KWW) function give $\beta_f = 0.92 \pm 0.03$ and $\beta_s = 0.68 \pm 0.05$ for PF2 and PF3 and we suggest that the non-exponential shape of the experimental correlation functions is caused by a distribution of molecular sizes and hence of molecular weights. This effect is not surprising since these samples have the considerable polydispersity that is usually found in thermally polymerized polymers. Two hydrodynamic modes are observed, a fast and a slow one. The relaxation rate of the fast mode is proportional to the square of the scattering vector, q , characteristic of diffusional dynamics. From

the position of the peaks we obtain the translational diffusion coefficient, D , and hence the equivalent hydrodynamic radius, R_h , using the Stokes–Einstein equation

$$R_h = \frac{kT}{6\pi\eta_0 D}, \quad (4)$$

where η_0 is the solvent shear viscosity and k_B is the Boltzmann constant. As this equation is valid in the limit of $c \rightarrow 0$ the numbers calculated from Eq. (4) are apparent hydrodynamic radii. The extrapolated quantity $(D\eta/T)_{c \rightarrow 0}$ is used in Eq. (4) to obtain the hydrodynamic radius, R_h , which is 4.2 ± 0.2 nm for the parent polymer, 7.0 ± 0.3 nm for PF2 and 8.2 ± 0.3 nm for PF3. Fig. 2 shows the evolution of the ILTs of the experimental correlation functions with time in pH=9. The distribution of decay rates shows two resolved peaks. There is a shift of the faster peak to shorter times as time progresses.

4. Discussion

These polymers which are characterized by the bulky hydrophobic NAA aromatic groups clustered toward the center of the coil and the hydro-

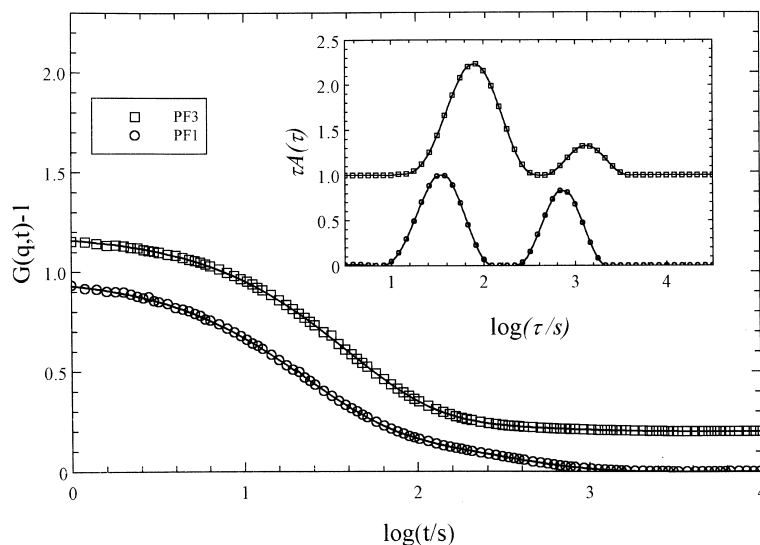


Fig. 1. Experimental correlation functions for PF1 and PF3 in pH=9. The inset shows the evolution of the distributions for the experimental correlation functions using REPES.

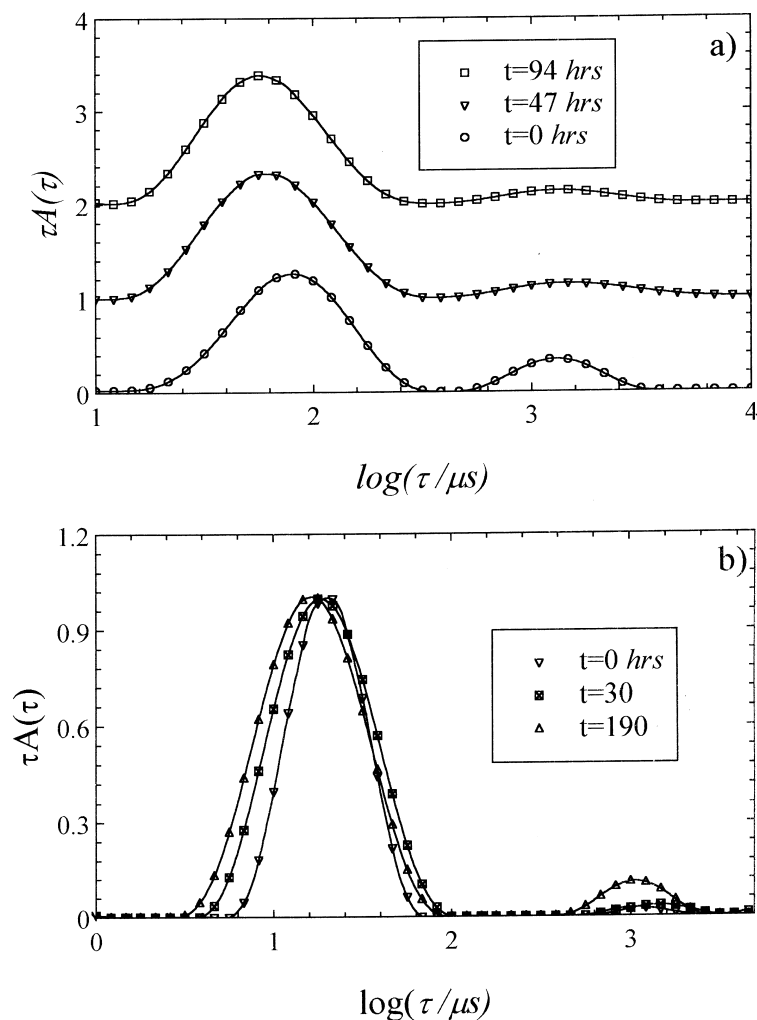


Fig. 2. (a) Shift of the fast mode to shorter times after hydrolysis for PF3 at $c = 0.0093$ g/ml. (b) Shift of the fast mode to shorter times after hydrolysis for PIBA3 at $c = 0.0096$ g/ml.

philic polar groups located in the aqueous boundary have been reported [16–20] to exist in dilute solution as “hypercoils”. The incorporation of the hydrophobic naphthyl group affects the size of the parent polymer. The hydrodynamic radius R_h which is 4.2 ± 0.2 nm for the parent polymer PF1, increases to 7.0 ± 0.3 nm for PF2. By increasing even more the amount of the hydrophobic substituent in PF3 the hydrodynamic radius becomes 8.2 ± 0.3 nm. We suggest that the large increase in the hydrodynamic size is caused by aggregation of individual chain molecules to form

multimolecular clusters. We propose, therefore, that under these conditions the polymers form an interior region containing a higher concentration of the hydrophobic aromatic NAA groups surrounded by an outer region of the hydrophilic acrylamide groups. Fig. 3 shows the changes in the apparent R_h of the NAA and IBA polymeric esters during hydrolysis at different times. Due to the apparent loss of the bulky bioactive residues the R_h of the aggregates in solution decreases as time progresses. As the hydrophobic core is losing its NAA substituents, the hydrophobic

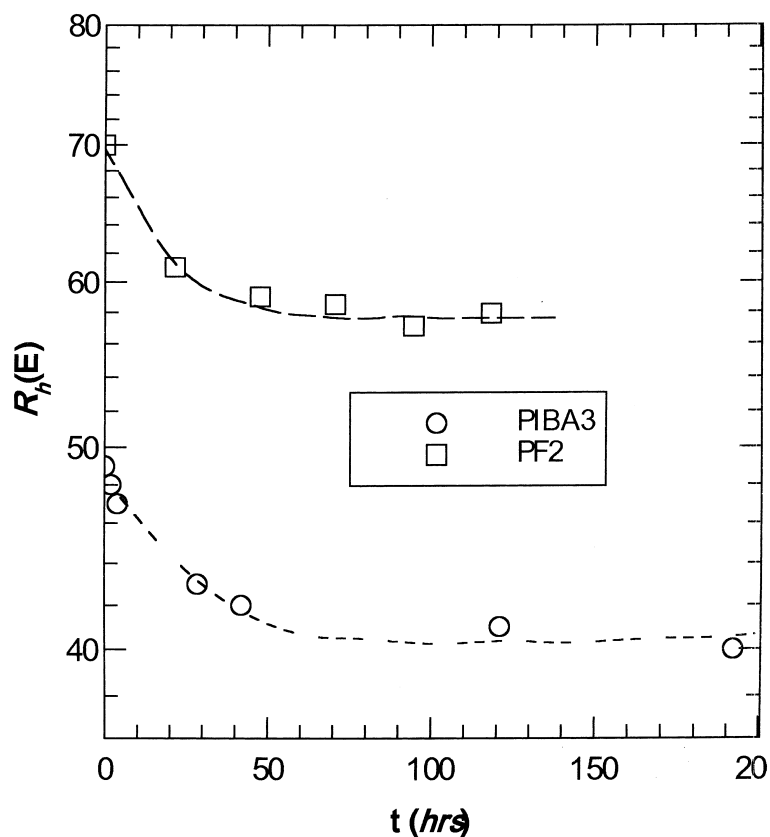


Fig. 3. The changes in the apparent hydrodynamic radius R_{ha} of (a) the PF2 and (b) the PIBA3 polymeric esters during hydrolysis as a function of time at pH=9 in 1% solution. The errors for the R_{ha} are within the size of the symbols displayed in the figure.

interactions inherent within the polymer decrease with a concomitant change in the conformation adopted by the respective polymer coils, that have now increased in size. Therefore the aggregates lose their stability in solution and begin to dissolve breaking into smaller aggregates. The occurrence of interpolymeric aggregation would be restrained as hydrolysis proceeds and finally after infinite time the hydrodynamic radius of the fully hydrolyzed polymer will become comparable to the R_h of the parent polymer. Indeed the current R_h s corroborate the above expected result.

In contrast the hydrodynamic radius R_h of the polymers with the IBA groups becomes 4.3 ± 0.2 nm for PIBA1, 4.4 ± 0.2 nm for PIBA2 and 4.7 ± 2 nm for PIBA3. We suggest that, these results of the light scattering experiments show that the incorporation of the IBA groups does not af-

fect the size of the parent polymer. The different behavior is caused by the smaller degree of aromatic character of the IBA linkages as compared to the increased hydrophobic character of the NAA side groups, since the IBA linkages have moderately polar character.

5. Conclusion

The hydrodynamic radius, R_h , of the parent polymer, almost doubles by incorporating the NAA linkages, but it remains approximately the same when the NAA linkages are replaced by IBA side groups of less aromaticity. The hydrodynamic radii and scattering intensities display a systematic decrease as a function of time apparently due to the loss of the NAA and IBA linkages

during hydrolysis. The obtained data concerning the properties of the macromolecular structures in solution lead the way toward a deeper understanding of the complex molecular phenomena occurring in solutions of hydrophobically modified polymers.

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