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SHORT COMMUNICATION

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Dynamic light scattering experiments on thermoreversible pregels from chemically modified PVC

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Abstract Dynamic light-scattering experiments have been performed on solutions of poly(vinyl chloride) (PVC) and chemically modified PVC (HPVC) in diethyl oxalate (DEO). Hydrodynamic sizes of the clusters in the solution were measured as a function of temperature, concentration and quenching temperature.

The higher the starting concentration of the PVC and HPVC solutions the larger the size of the aggregates formed. However, clusters formed by pure PVC are smaller than those formed by modified PVC. Aggregate sizes decrease with increasing temperature whereby a change in the cluster melting process is observed at 55 °C. Successive dilution of highly concentrated aggregate solutions causes reduction of the cluster size until a critical dilution concentration is reached below which no further reduction in size occurs. The lower the temperature at which the solutions are quenched the larger the clusters which are formed.

We believe that all results can be interpreted using a model developed by Guenet [1–4] which describes the molecular structure of PVC/DEO gels and pregels.

Key words Poly(vinyl chloride) – gelation – dynamic light scattering – hydrodynamic radius

Introduction

Since four decades when the gelation phenomenon of PVC was discovered it has been difficult to explain why a mainly atactic polymer like PVC can form gels exhibiting very high elastic moduli. In the last few years, considerable progress has been made in understanding the molecular structure and the mechanism of PVC gel formation [1–8]. Systematic studies using different techniques including scattering, mechanical, viscoelastic and calorimetric measurements of gels and pregels formed by PVC and modified PVC in different types of solvents have been performed [9–13]. These studies have led to the conclusion that PVC gels generally consist of cross-sectional polydispersed fibers whose stability is mainly achieved by crystallization of the syndiotactic regions of the polymer. In the case of solvents of type diester, a second kind of links exists and is thought to be due to the origin of the formation of a PVC–solvent complex in the less stereoregular sequences of the polymer. This complex can be formed by electrostatic interactions of the negatively polarized oxygen atoms of the solvent and the positively polarized hydrogens of the PVC.

Recently, average cluster molecular weights, z-average cluster radii of gyration and fractal dimensions of PVC/Diethyl oxalate (DEO) pregels have been determined by static light scattering measurements and compared with the data found in DEO solutions of chemically modified PVC [14]. This paper reports complementary experiments on the dynamic properties of the PVC/DEO and HPVC/DEO systems. The effect of temperature, concentration, dilution and quenching temperature on cluster dimensions is investigated by dynamic light scattering (DLS).

Experimental part

Materials

A PVC of commercial origin (Rhone Poulenc SA) was used without further purification. The weighed average molecular weight was 120 000 g/mol and the polydispersity index $M_w/M_n = 2.3$. Tacticity characterization of the polymer performed by ^{13}C-NMR gave the following proportion of triads: syndio: 33%, iso: 18%, hetero: 49%.

The modified PVC used in this study was obtained by gradually replacing some chlorine atoms of pure PVC by hydrogen using $LiAlH_4$ as the reducing agent. This reaction has the advantage to be stereospecific in the sense that only iso and heterotactic triads react while syndiotactic chlorines remain unaffected. Furthermore, it could be shown by ^{13}C-NMR that the resulting copolymers are random [15–16]. More details about the reaction and the characterization of the obtained products are described elsewhere [17, 18]. For the present study, PVC was reduced to yield modified PVC where 3% of the chlorine atoms are replaced by hydrogen (HPVC).

Diethyloxalate was purchased from Aldrich and was made dust-free by repetitive filtration through 0.1 μm micropore teflon filters.

Sample preparation

Solutions from PVC and HPVC in DEO with starting concentrations ranging from $c_p = 2$ to $16\,\mathrm{mg/cm^3}$ were prepared under stirring at 150 °C and then quenched at 25°C. Generally the samples were aged for at least 3 days prior to measurements.

Dynamic light scattering measurements

They were performed with an Argon Laser Lexel 85 ($\lambda = 488$ nm). The samples were temperature controlled at $\pm$ 0.1 °C within the range of 20 °–80 °C. The range of scattering wave vector in the light scattering experiment was $0.012 < q < 0.034\,\mathrm{nm}^{-1}$, where $q = 4\pi n/\lambda^* \sin\theta/2$, θ is the scattering angle, λ the wavelength of the laser and n the refractive index of DEO. The autocorrelation functions were performed with the digital correlator BI-9000 AT from Brookhaven Instruments Corporation. Analysis of the correlation functions was carried out using the first cumulant method where the average decay rate $\langle\Gamma\rangle$ is computed assuming a single decay exponential of the autocorrelation functions.

In order to determine the hydrodynamic cluster radius according to the Stokes–Einstein formula the absolute viscosities of DEO were measured as a function of temperature using the Ubbelohde capillary viscometer ISO 3105 of Schott.

Results and discussion

Effect of preparation concentration

The cluster dimensions of polymer solutions were obtained using dynamic light scattering by measuring the average decay rate of the first cumulant as a function of the scattering vector which is related to the translational diffusion coefficient D as $\langle\Gamma\rangle = Dq^2$. Assuming that the overall shape of the particle is sphere-like (this has been shown to be the case in PVC pregels) hydrodynamic radii R_H of the clusters can be calculated using the Stokes–Einstein relationship $D = kT/(6\pi\eta R_H)$ where k is the Boltzmann constant, T the temperature and η the absolute viscosity of the solvent.

In Fig. 1 the average decay rate of the first cumulant is plotted as a function of the square of the scattering vector for PVC/DEO pregels at different concentrations. The frequency is found to be q^2-dependent and shows the diffusive nature of the motion. From the slope of Γ vs. q^2 diffusion coefficients were calculated. The obtained values for PVC and HPVC solutions are plotted in Fig. 2 as a function of the starting concentration. As expected in both systems diffusion coefficients decrease with concentration. Furthermore, it can be seen than clusters from HPVC are larger than those formed in unmodified PVC pregels. The same tendency had already been found using the static light-scattering experiments where radii of gyrations of both systems were compared. The result can be interpreted using a model described by J.M. Guenet which accounts for the molecular structure of PVC/DEO gels and pregels. According to this model the aggregates are made up of fiber-like structures where the stability is mainly achieved by crystallization of the syndiotactic regions of the polymer and also by the formation of

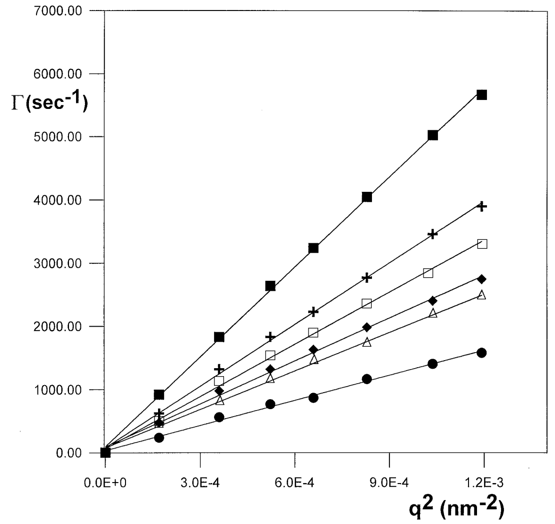


Fig. 1 Decay rate of the first cumulant as a function of the scattering vector for PVC/DEO solutions at different preparation concentrations c_p; $c_p = 16$ mg/ml (●), 12 mg/ml (△), 10 mg/ml (◆), 7.5 mg/ml (□), 5 mg/ml (+), 2 mg/ml (■)

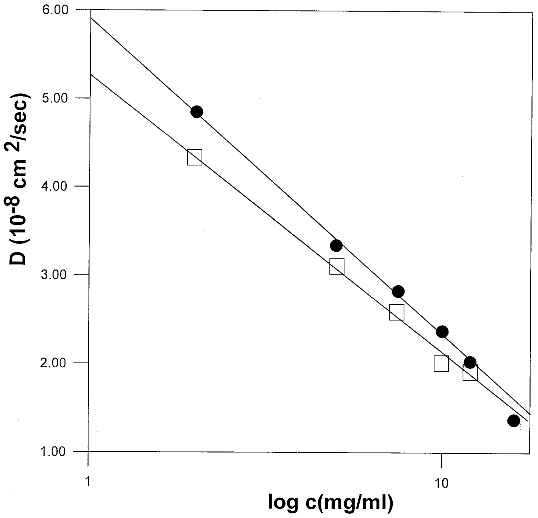


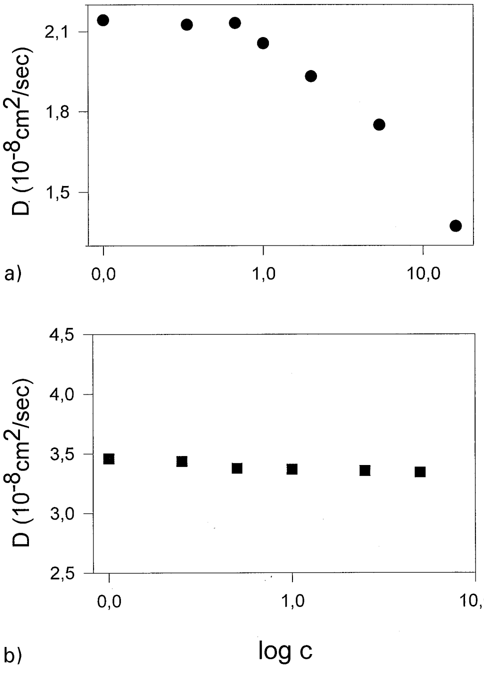
Fig. 2 Semi-logarithmic representation of the translational diffusion coefficient as a function of the preparation concentration c_p in pregels from PVC (●) and HPVC (□)

PVC-DEO complex in the less stereoregular sequences. Whenever a chlorine atom of PVC is substituted by a hydrogen no complex can be formed at this site and chain–chain interactions are reduced. As a consequence clusters formed by modified PVC should swell stronger and yield larger hydrodynamic radii than those of pure PVC.

Effect of dilution on particle size

As has been shown in a recent work, radii of gyrations of PVC clusters are accessible by static light-scattering measurements when solutions of starting concentrations are diluted infinitely. This, however, assumes that the crystalline links, which mainly determine the stability of the fibers, are stable and also the clusters do not break up upon dilution. In order to verify this assumption, PVC/DEO solutions at different starting concentrations were successively diluted and hydrodynamic radii measured after each dilution. As shown in Fig. 3 two types of behaviors can be distinguished. For the starting concentrations $c_p = 16$, 12, 10 and 7.5 mg/ml, successive dilutions yield an increase of the diffusion coefficient until a critical dilution concentration is reached below which the value for D remains constant (Fig. 3a). On the other hand, for the low starting concentrations, i.e. 5 and 2 mg/ml (Fig. 3b), dilution does not have any influence on D and on the hydrodynamic radius. To explain these results we have to consider that aggregates formed at high preparation concentrations are relatively large and strongly interconnected. The interconnections have been shown to be made up of polymer–solvent links which are much weaker than crystalline interactions. When diluting these solutions the weak links are destroyed until a certain concentration is reached where all interconnections have disappeared and

Fig. 3 Semi-logarithmic representation of the translational diffusion coefficient as a function of dilution concentration in a PVC/DEO pregels of (a) $c_p = 16$ mg/ml (●) and (b) $c_p = 5$ mg/ml (■)



only individual clusters are present. As the stability of these clusters relies essentially on the existence of crystallites in the syndiotactic sequences of the PVC chains and further dilution does not yield in any further reduction of the aggregate size it is thus believed that the above hypothesis, where it was assumed that clusters do not break up upon dilution, is correct.

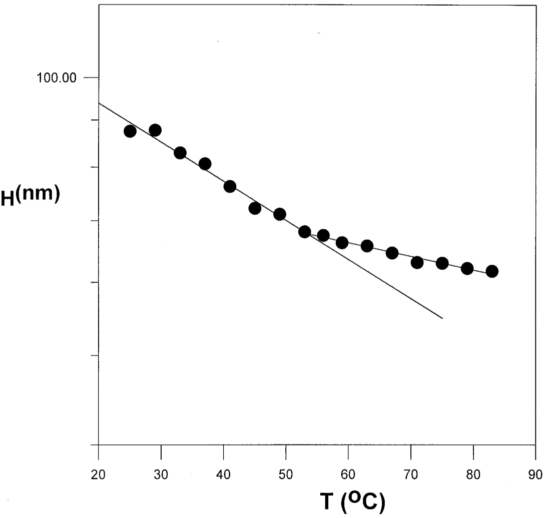
On the other hand, clusters in solutions at low starting concentration are relatively small and therefore it is not surprising that no effect of dilution is observed. Obviously, in these solutions only single aggregates, which are not interconneted, are present.

Effect of temperature on cluster size

To study the effect of temperature on the cluster size of a PVC/DEO solution the autocorrelation function of an aged sample of preparation concentration $c_p = 16$ mg/ml was measured at temperatures between 25 and 80 °C. After each measurement the temperature of the sample was increased and waited 30 min until the system was in equilibrium prior to the experiments. From the diffusion coefficients obtained by the autocorrelation measurements the hydrodynamic radius of the clusters can be calculated using the Stokes–Einstein formula when the viscosity coefficients of the solvent at each temperature is known. Viscosities were measured in an Ubbelohde viscometer at different temperatures.

The resulting hydrodynamic radii as a function of temperature are presented in Fig. 4 in a semi-logarithmic plot. As can be seen R_H decreases with temperature which means that clusters become smaller. At about 55 °C the slope of the curve changes which indicates a change in the cluster melting process. This result is not surprising when considering the data of calorimetric measurements on gels from PVC in diester solvents. Indeed, DSC curves of these systems have shown the presence of two endotherms [19]. A strong one at about 110 °C which was attributed to the disappearance of the syndiotactic crystals and a weaker one between 50 and 60 °C which has been interpreted to be due to the existence of a polymer–solvent complex. So, by increasing the temperature between 25 and 55 °C the aggregate size reduces due to the "melting" of both types of links. At 55 °C polymer–solvent compound connections are completely molten and at temperatures above 55 °C further reduction of the particle size occurs only by disaggregation of the crystalline links. Therefore, the slope at $T > 55$ °C is smaller than that in the low-temperature range.

Fig. 4 Semi-logarithmic representation of the hydrodynamic cluster radius as a function of temperature in a PVC/DEO pregel of $c_p = 16$ mg/ml



Effect of quenching concentration on particle size

Another parameter which strongly influences the cluster size is the quenching temperature at which PVC solutions are cooled down and where pregel formation takes place. This effect can be quantified experimentally by the study of the kinetics of aggregate formation. Solutions of PVC/DEO and HPVC/DEO at starting concentration $c_p = 16$ mg/ml were heated up to 150 °C in the measuring cell and then directly quenched into the thermostated vat liquid of the goniometer. As PVC/DEO is a strong scatterer stable correlation functions are obtained after 20 s.

Figure 5 shows a plot of the average decay rate of the first cumulant measured at an angle of 90 ° as a function of time. The fact that this kind of representation yields straight lines in all cases shows that the kinetic of aggregate formation follows an exponential law. Chain aggregation is very rapid in the early stage and remains nearly unaltered after about 40 min. On the other hand, it follows from Fig. 5 that an increase of the quenching temperature yields in the formation of smaller aggregates for both, PVC/DEO and HPVC/DEO solutions. Comparing the two systems at the same temperatures confirms what has been already discussed above: clusters formed by HPVC are larger than those of the unmodified PVC.

The finding that lower quenching temperatures cause the formation of larger aggregates can be explained by the fact that polymer crystallization which is responsible for gel formation in the early stage is a nucleation-controlled process. The steady-state nucleation rate generally applicable to all nuclei types and shapes is given by

$$N = N_0 \exp[-(E_D + \Delta G^*)/RT] ,$$

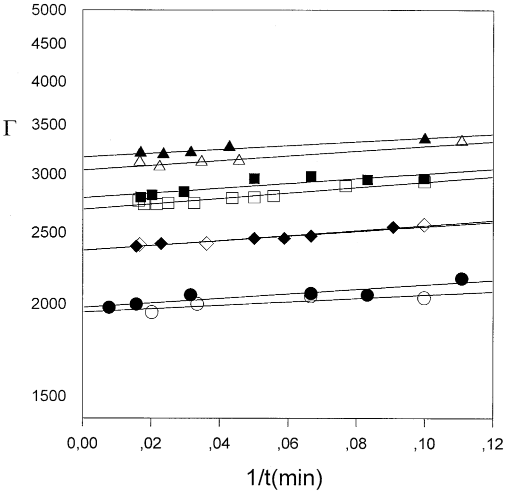


Fig. 5 Semi-logarithmic representation of the decay rate as a function of aggregate formation time at different quenching temperatures T (●, $T = 20\,^\circ\mathrm{C}$; ◆, $T = 30\,^\circ\mathrm{C}$; ■, $T = 40\,^\circ\mathrm{C}$; ▲, $T = 50\,^\circ\mathrm{C}$) filled symbols: PVC/DEO solutions; empty symbols: HPVC/DEO solutions

where N is the number of nuclei formed, ΔG^* the free energy necessary to form a nucleus of critical size, E_D the free energy of activation for transport across the liquid–nucleus interface and T the crystallization temperature. This expression shows qualitatively that a polymer solution quenched to low temperatures contain less nuclei than a solution in which crystallization takes place at higher temperature. As a consequence, in one case few large crystals grow while in the other case more but smaller ones are present.

Conclusions

The dynamic light-scattering experiments presented in this paper have shown that the cluster dimensions of PVC/DEO solutions depend on different parameters like the starting concentration of the solutions, dilution concentration, temperature and quenching temperature. All results found in this investigation are consistent and give further support to the polymer–solvent complex model of Guenet for gelation of PVC.

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