Evidence for Preferential Polymer Solvation from Time-resolved Rayleigh Light Scattering Measurements

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In an acetone solution containing small portions of naphthalene the latter is adsorbed preferentially to poly(methylmethacrylate-co-phenylvinylketone). Evidence for preferential solvation is inferred from intrinsic viscosity data as well as from the halflife of the change of light scattering intensity after fragmentation of the macromolecules by a 25 ns flash of 347 nm light from a ruby laser.

Recently a device has been developed in our laboratory in order to investigate the kinetics of polymer degradation in solution with the aid of Raleigh light scattering in conjunction with pulse radiolysis and laser flash photolysis [1]. By this method the separation of fragments of macromolecules generated by main chain scission can be monitored. If the time to accomplish a bond rupture is sufficiently short, the diffusion of the fragments is the rate determining step with respect to the observed change of light scattering intensity (LSI). This kind of behavior was found for various polymers such as polyphenylvinylketone (PPVK) [1] and polyisobutene [2].

During the investigation of copolymers of phenylvinylketone (PVK) and methylmethacrylate (MMA) the following observation was made: If acetone solutions of the copolymer containing naphthalene were irradiated with laser flashes ($\lambda = 347.1$ nm, flash width: 25 ns) the half life of decay of LSI $\tau_{1/2}$(LSI) increased with increasing naphthalene concentration. Figure 1 shows that $\tau_{1/2}$(LSI) approaches a limiting value at naphthalene concentrations greater than 0.05 M. Measurements at naphthalene concentrations above 0.1 M were not possible as naphthalene also quenches the main chain degradation. Other quenchers for PVK triplets such as 2,5-dimethylhexadiene-2,4 also diminished the extent of degradation but did not exert any influence on $\tau_{1/2}$(LSI).

Principally the lifetime τ(LSI) can be correlated to the lifetime of an intermediate leading to main chain rupture or to the diffusion time of the fragments. The latter will be the case if the lifetime of the intermediate is much shorter than the diffusion time. In this work evidence has been obtained that the observed relaxation time is due to a diffusion process as will be reported in detail elsewhere [3]. It should only be mentioned here that $\tau_{1/2}$(LSI) is expected to decrease with increasing naphthalene concentration if it were related to a chemical act which is influenced by naphthalene. However, the inverse effect of naphthalene concentration on $\tau_{1/2}$(LSI) has been observed.

As experienced so far with other polymers $\tau_{1/2}$(LSI) values related to diffusion increase linearly with microviscosity (viscosity of the solvent). By adding naphthalene to acetone up to a concentration of 0.1 M the viscosity increases only by a factor of 1.04. Thus, the effect demonstrated in Fig. 1 certainly is not due to a change of microviscosity.

Therefore, it is concluded that the observed influence of naphthalene on $\tau_{1/2}$(LSI) is due to preferential solvation of macromolecules by naphthalene molecules. This means that bulky naphthalene molecules attached to macromolecules reduce the mobility of the latter significantly thus increasing the time of fragment separation. This assumption is confirmed by the fact that $\tau_{1/2}$(LSI) is approaching a limiting value.

In order to gain evidence of preferential solvation of the polymer by naphthalene in the system under investigation by another method, the intrinsic viscosity of the copolymer in acetone $[\eta]$ and in acetone containing 0.1 M naphthalene $[\eta]_{\text{Naph}}$ was measured at room temperature. The coefficient of preferential solvation λ/C was calculated according to the following relationship reported by Dondos [4]:

$$\lambda/C = 1/[\eta]_{\text{Naph}} - 1/[\eta] . \tag{1}$$
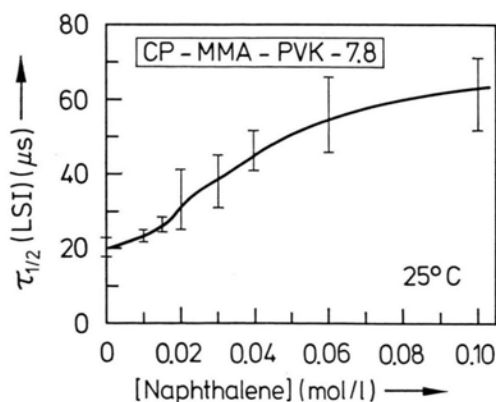

Fig. 1. $\tau_{1/2}$(LSI) versus the concentration of naphthalene added to an acetone solution of a poly(methylmethacrylate-co-phenylvinylketone) sample containing 7.8 mol% PVK (0.021 base mol/l). Absorbed dose per flash: 8.4×10^{-5} einstein/l.

With $[\eta]_{\mathrm{Naph}} = 160$ ml/g and $[\eta] = 141$ ml/g $\lambda/C = -8.4 \times 10^{-3}$ g/ml is obtained. The negative sign of λ/C demonstrates that naphthalene is adsorbed pre-ferentially to the polymer as was concluded from the dependence of $\tau_{1/2}$(LSI) on the naphthalene concentration.

[1] G. Beck, J. Kiwi, D. Lindenau, and W. Schnabel, Eur. Polym. J. **10**, 1069 [1974].

[2] G. Beck, D. Lindenau, and W. Schnabel, Eur. Polym. J. **11**, 761 [1975].

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[4] A. Dondos, C. R. Acad. Sci. Paris, C **272**, 1419 [1971].