produce an emission lifetime characteristic of an unquenched chromphore. The relatively short value of τ_3 observed in the current work might suggest that such a mechanism does not hold for PNMA although further work e.g. with copolymer series in which individual rate constants could be examined would be necessary to clarify the situation.

As for P1VN and P2VN the value of τ_2 associated with the monomeric entity involved in energy migrative population of excimer sites is short as is to be expected in such a kinetic scheme.

Conclusions

The kinetic schemes proposed on the basis of studies of the intramolecular concentration dependence of excimer formation in a variety of copolymer systems appear to be valid for the aromatic homopolymers studied. Consequently, analysis of fluorescence data in terms of the direct application of the Birks kinetic scheme must be viewed with caution.

Acknowledgements

Financial assistance from the Science Research Council, the Royal Society and the U.S. Army European Research Office is gratefully acknowledged.

The authors wish to acknowledge useful discussions with Professors J. E. Guillet (University of Toronto) and F. C. De Schryver (University of Leuven).

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Experimental studies of poly(vinyl acetate) networks swollen in isopropyl alcohol below the θ-temperature

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(*Received* 14 *November* 1980; *revised* 6 *January* 1981)

Introduction

At the θ-temperature the repulsive and attractive forces balance each other, and the mean size of a polymer molecule is that of a random coil. Below the θ-temperature the attractive forces predominate, and a phase transition of polymer networks marked by a sudden change in the degree of swelling has been theoretically predicted[1–3]. Although this phenomenon attracted attention in the past and is still the subject of many theoretical discussions, only a small number of experimental studies have been reported[4–7].

Experimental

Various poly(vinyl acetate) networks were prepared according to a previously described method[8]. The crosslinking density which is the average number of crosslinks on a primary chain was varied from 5 to 72. Several series of networks have been prepared differing from each other not only in their crosslinking densities (l) but also in the initial polymer concentration (c_0) at which the crosslinks were introduced (3, 6, 9 wt%).

Cylindrical gel pieces and films were prepared for the optical and swelling degree measurements. The swelling degree, that is the ratio of the total mass of the swollen gel to that of the dry polymer within the network, was determined by weighing the samples after 2 weeks at each temperature in order to obtain the equilibrium swelling degree of the network.

Turbidity measurements were carried out by a BRICE PHOENIX universal light scattering photometer. The turbidity of the films was determined at a wavelength of 546 nm as a function of the temperature which was measured nearby the gel samples by a platinium resistance sensor connected to a KNAUER universal

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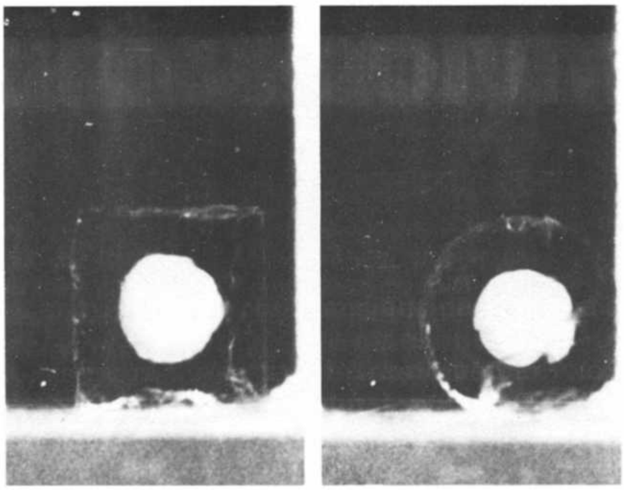

Figure 1 Typical separated network (l = 72, c_0 = 3 w%) which has been stable for 3 years at room temperature

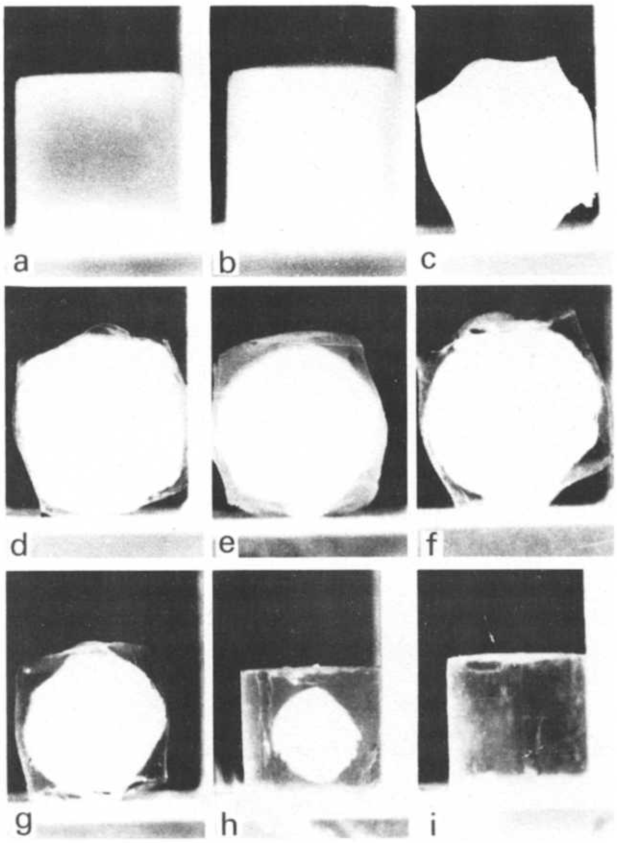

Figure 2 Formation and disappearance of the structure (l = 40, c_0 = 6 w%). a, 5 s; b, 120 s; c, 10 days; d, 22 days; e, 28 days; f, 36 days; g, 45 days; h, 87 days; i, 131 days

temperature measuring instrument. The intensity of the transparent light as a function of temperature was recorded by a HUSTOW 2000 X-Y recorder. The speed of cooling was fast enough to prevent deswelling of the gels, thus during the cooling process the concentration of the network could not change. Different concentrations for a given network were established by maintaining swelling equilibrium with pure solvent at different initial temperatures. The cloud points (the temperatures at which a sharp decrease of the intensity of the transparent light was detected) were determined at different polymer concentrations. The θ-temperature of the solutions was determined by the Shultz-Flory plot and was found to be 54.7°C.

Results and discussion

Both types of samples (films and cylinders) show very significant changes at a temperature below the θ-temperature. As a consequence of cooling the originally transparent gels became turbid. At this temperature the swollen network is no longer in equilibrium with the surrounding diluent, the concentration of the polymer increases (i.e. the swelling degree decreases), and two macroscopically observable phases appear. With cylindrical samples a separated network structure which consists of a transparent crust and a sphere-like turbid core has been observed. *Figure 1* shows a typical separated network and *Figure 2* illustrates the formation of such a structure. After the appearance of the transparent crust the originally well-shaped sample is distorted because the turbid bulky phase relaxes more slowly than the crust. At later times the radius of the turbid sphere keeps on decreasing until it reaches a limiting value (*Figure 1*) or completely disappears (*Figure 2*). Having reached the new swelling equilibrium the distorted gels become well-shaped again.

Collapse of the gels has not been observed (*Figure 3*), although the network chains in the turbid sphere could be supposed to be in a collapsed state. It seems that the difference in the initial polymer concentration does not affect the cloud points of the networks considerably. It is an open question yet, whether the differences in the cloud points are due to different crosslinking densities or to different polymer concentrations which result from the different crosslinking densities. The dependence of the cloud points on the polymer concentration of one of our samples can be seen on *Figure 4*. The remaining turbidity

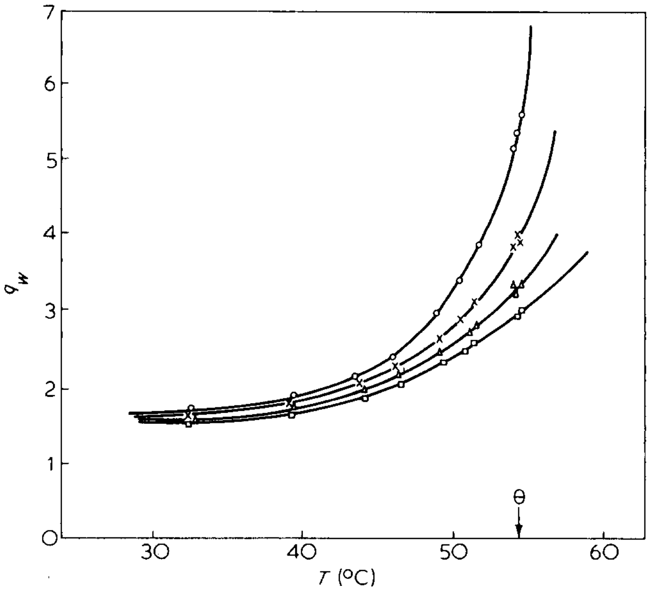

Figure 3 Equilibrium swelling degree of different networks as a function of temperature q_w is the ratio of the total mass of the swollen gel to that of the dry gel (c_0 = 9 w%; l = ○, 10; x, 20; △, 30; □, 40)

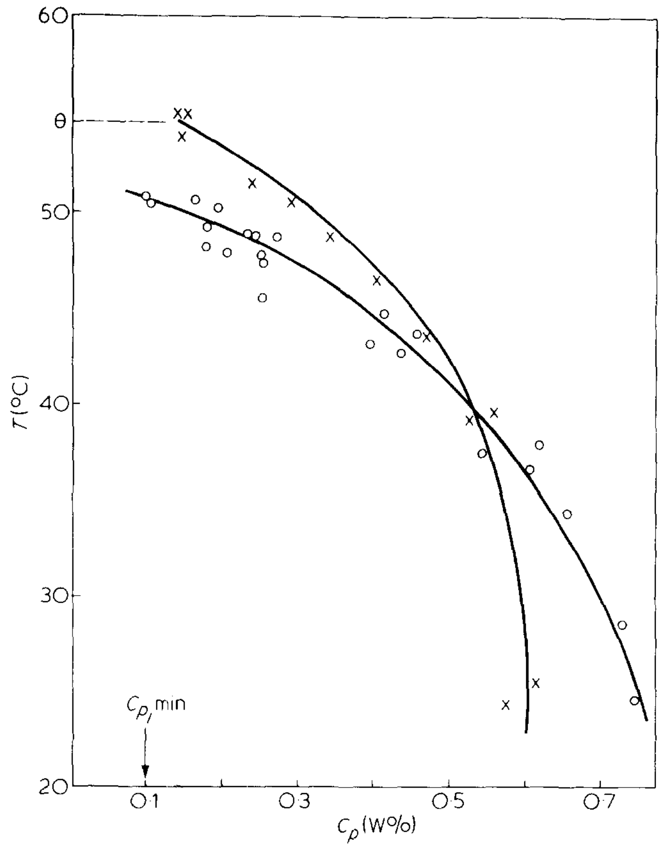

Figure 4 The cloud points curve (O) and the dependence of the equilibrium polymer concentration (x) on the temperature. C_p is the polymer concentration of the swollen gel and C_{p_l} min represents the minimal concentration at which the network structure still exists (l = 10, c_0 = 6 w%). The lines are guides for the eye

of some samples can be understood if we compare the cloud points curve with that of the equilibrium concentration curve. It can be seen that there is a certain region of a stable separated network at temperatures below the intercept.

The films show quite different structures which are more disperse than those of the cylinders, but the crust can also be seen here. Experiments to obtain more information about the molecular structure of the turbid sphere and to determine the spinodal temperatures are in progress.

Acknowledgements

We should like to thank Dr M. Nagy for providing us with useful information for preparation of the samples. Thanks are due to Professor E. Wolfram for helpful discussions, and to Dr I. Tar for continuous encouragement and stimulating comments.

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Substrate selectivity effects involving polymer-supported phase transfer catalysts

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Introduction

The use of polymer resins as supports for catalysts and reagents has increased enormously over the last few years and from time to time there have been reports of so-called 'substrate selectivity' effects, i.e. circumstances when a resin-bound reagent displays a higher reactivity for one substrate relative to another, over and above that observed with the analogous non-supported reagent[2,3]. Depending upon the magnitude of this effect and the particular substrates and reactions involved, such phenomena could of course have considerable commercial significance. Substrate selectivity might arise from a specific interaction of one substrate with a binding site close to a reactive centre as with enzymes. However, with resin-supported reagents, it might in principle arise from (i) less specific thermodynamic factors, in that one substrate may be sorbed into the resin in preference to another, or (ii) kinetic factors when one substrate may diffuse more rapidly into a resin than another. These two cases might be distinguished as 'thermodynamic substrate selectivity' and 'kinetic substrate selectivity'. We have previously established the criteria for the latter effect to manifest itself in the case of alkyl halides reacting with resin-supported pyridine groups[4]. In general, the inherent rate of the chemical reaction at sites within the resin must be rapid in comparison with the rate at which substrates diffuse from the bulk reaction medium. Under these circumstances a concentration gradient will be maintained across the resin interior, and substrates will react according to their rates of diffusion and not their inherent chemical reactivities[5]. In general, of course, larger substrates will diffuse more slowly than smaller ones and hence their overall relative reactivity is more likely to be reduced. In addition, less porous resins, e.g. more highly crosslinked ones, are more likely to provide the conditions for diffusion to become rate controlling. In the case of ion exchange resins all of these factors have been considered before and have been very elegantly treated[6]. However, these principles are only now being adequately

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