

Diffusion and Intermolecular Reaction Rates of End-Labeled Polystyrenes in Polymer Networks Studied with Triplet Probe

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SUMMARY

The effect of chemical network on the diffusion and reaction rates of end-labeled polystyrenes in semidilute region has been measured by phosphorescence quenching technique with a 10-ns nitrogen-laser pulse, and is discussed in comparison with the results for linear polystyrene solution. The quenching rates between end-labeled polymers in semidilute region are influenced much by the formation of chemical crosslinks between the inert polymer chains.

INTRODUCTION

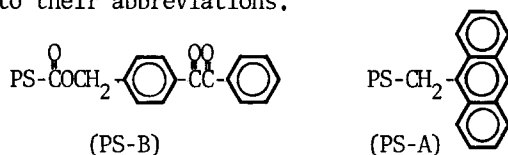
Luminescence spectroscopy is a powerful research tool in the study of structure, mobility, and reaction of both synthetic and biological macromolecules (MORAWETZ 1979). Information from the excited-triplet-state is of special importance, since its longer lifetime allows us to study mobility and reactions reflecting the large scale motions of the whole polymer chains in solution. The quenching rates k_q of phosphorescence of polystyrylbenzil (PS-B) by polystyrylanthracene (PS-A) in benzene, cyclohexane, and butanone at 20-40°C have already been studied in both dilute (HORIE et al 1977, 1978) and in semidilute (MITA et al 1979) regions, by using a 10-ns dye-laser (406nm) or nitrogen-laser (337nm) pulse.

The diffusion of small molecules and polymers in polymer networks is an important process to be considered, when we use crosslinked polymers as support materials for various catalysts, organic reagents as well as beads for gel permeation chromatography. The hydrophobicity and dynamic characteristics of crosslinked polystyrene beads have recently been studied with fluorescent probes (HORIE et al 1980).

In the present work, by using the triplet probe, we measure the quenching rate constants k_q of PS-B by PS-A in swollen polystyrene networks (PSN) in benzene, and discuss them in comparison with the k_q in semidilute solution of linear inert polystyrene (PS) in benzene.

EXPERIMENTAL

Substantially monodisperse PS-B and PS-A were prepared by anionic polymerization as previously reported (HORIE 1977). The numbers of monomer units in polystyrene chains are indicated by figures added to their abbreviations.



The polystyrene networks (PSN) were prepared by radical copolymerization of styrene with divinylbenzene (DVB) in benzene with AIBN ($1.2 \times 10^{-3} \text{M}$) at 50°C for two weeks. The mole fraction of DVB, m_D , was set constant ($m_D=0.02$) in all preparation experiments, and the effective crosslinking density, ν , was changed by changing the weight fraction ω of the monomer mixture in the copolymerization solution.

The phosphorescence decay curves for degassed and sealed samples in Pyrex-glass tube at $20\text{--}40^\circ\text{C}$ were measured with 10-ns nitrogen-laser pulse and transient-time converter. The range of the concentration of benzil group was $2 \times 10^{-4} \sim 1 \times 10^{-3} \text{M}$. The other detailed procedures for the measurements were the same as reported (HORIE 1977). The bimolecular rate constant k_q was calculated from

$$1/\tau = 1/\tau_0 + k_q[A], \quad (1)$$

where τ and τ_0 are triplet lifetimes of the benzil group in the presence and absence of quencher, respectively, and $[A]$ is the concentration of anthryl group.

RESULTS AND DISCUSSION

Characterization of Polystyrene Networks

The equilibrium swelling degree Q for the polystyrene network (PSN) was measured with benzene and converted to ν in mol/cm^3 of dry gel by

$$\nu = \frac{1}{2N_c V_{02}} = \frac{(0.5 - \chi)Q^{-5/3}}{2V_{01}(Ah^{2/3} - BQ^{-2/3})} \quad (2)$$

TABLE 1. Preparation Conditions and Characteristics of Polystyrene Networks

Crosslinked polymer	m_D	ω	Q	N_c	$\nu \times 10^4, (\text{mol}/\text{cm}^3)$	$\nu_{\text{ent}} \times 10^4, (\text{mol}/\text{cm}^3)$
PSN96	0.02	0.20	11.0	96	0.54	--
PSN45	0.02	0.30	7.0	45	1.14	--
PSN35	0.02	0.40	6.0	35	1.47	--
PSN21	0.02	0.60	4.4	21	2.46	0.39

where N_c is the number of monomer units between crosslinks, and other symbols are the same as originally given (HERTZ et al. 1978). The values of $A=0.5$, $B=0$, and $h^2/3=0.5$, together with $\chi=0.37$ (ALTARES et al 1964) were used. The results are shown in TABLE 1. The crosslinking density due to physical entanglement $\nu_{ent} = \nu - \nu_{chem}$ was also estimated by using the crosslinking density by DVB, $\nu_{chem} = 2.1 \times 10^{-4} \text{ mol/cm}^3$.

Rate Constants between PS-B and PS-A in Linear PS Solution

The results from the quenching rate constants k_q of PS-B by PS-A in benzene in the presence of linear standard polystyrene having a similar number of monomer units, N (MITA 1979) are reproduced in Fig. 1.

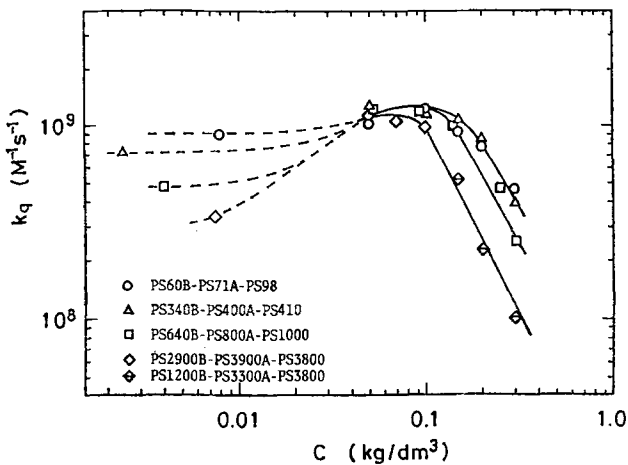


Fig. 1. k_q in linear PS solution at 30°C against C .

First, in spite of the increase in viscosity of the solution with increase in polymer concentration, C , k_q does not decrease but rather increase somewhat until C reaches about 0.05 kg/dm^3 . Second, for $C=0.05 \text{ kg/dm}^3$, k_q is independent of N within the experimental error. Third, k_q begins to decrease with the further increase in C . This critical point appears earlier for systems with larger N , and roughly corresponds to the overlap concentration C^* denoting the cross-over from dilute to semidilute region. Fourth, the slope for the straight lines in semidilute region in Figure 1 is $-1.7 \sim -1.9$. This value coincides with the prediction of $D_{self} \propto C^{-1.75}$ by de Gennes' dynamic scaling theory with a reptation model (DE GENNES 1976, 1979).

Rate Constants between PS-B and PS-A in PS Networks

The quenching rate constants k_q of PS-B by PS-A and k_q for their model reaction between benzil and anthracene in swollen

TABLE 2. Quenching Rate Constants k_q and Reduced Rate Constants $k_q \eta_0 / T$ between PS-B and PS-A in Swollen Polystyrene Networks (PSN) in Benzene

Phosphoro- phore	Quencher	Cross- linked polymer	C (kg/dm ³)	$k_q \times 10^{-9}$ (M ⁻¹ s ⁻¹)			$k_q \eta_0 / T$ (J/K·mol)
				20°C	30°C	40°C	
Benzil	Anthracene	PSN96	0.072	3.45	3.50	3.02	6.06
		PSN35	0.18	0.88	1.09	1.44	2.08
		PSN21	0.26	0.51	0.56	0.68	1.08
PS60-B	PS71-A	PSN96	0.12	0.75	0.63	1.18	1.56
		PSN45	0.17	0.71	0.58	0.67	1.25
		PSN21	0.27	0.28	0.26	0.47	0.61
PS210-B	PS400-A	PSN96	0.13	0.50	0.57	0.65	1.06
		PSN45	0.18	0.44	0.49	0.90	1.10
		PSN21	0.25	0.33	0.36	0.41	0.69
PS1200-B	PS800-A	PSN45	0.18	0.15	0.16	0.20	0.31

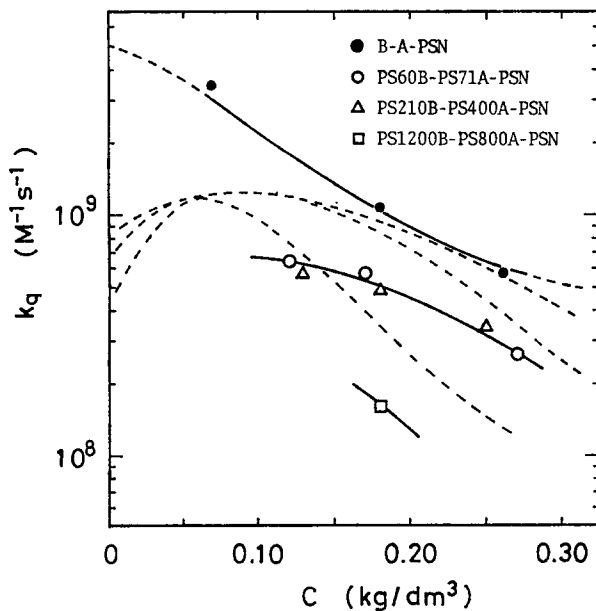


Fig. 2. Rate constants k_q in PSN at 30°C against polymer concentration C . Dotted lines correspond to k_q in linear polystyrene solution.

polystyrene networks (PSN) in benzene are summarized in TABLE 2 and shown in Fig. 2 against polymer concentration C for 30°C. The values of k_q for corresponding reactions in linear polystyrene solutions are also shown by dotted lines. The total concentration of polymers, C , was chosen, so that PSN could sufficiently swell the benzene solution of PS-B and PS-A.

The k_q for the diffusion-controlled reaction between the small molecules in PSN decreases with increasing C , and agrees well with k_q between benzil and anthracene in linear polystyrene solution (HORIE 1976) of the same C . The rate constant k_q can be related to the diffusion coefficient, D , by using a modified Smoluchowski equation (HORIE 1977)

$$k_q = 8\pi\gamma RD \quad (3)$$

with the radius of triplet-triplet energy transfer $R=1.37$ nm (HORIE 1978) and the steric hindrance factor $\gamma=1$. So, it is clear that the diffusion of small molecules is influenced much by the existence of polymer chains, but is not affected by the formation of chemical crosslinks between polymer chains.

The k_q for polymer-polymer reactions in PSN decreases with increasing C , in a similar manner as k_q in linear PS solution, but the absolute values are quite small compared with the latter. The difference becomes more marked as the diffusing molecule has a larger number of monomer units, N , as is shown in Figure 3. The rate constants k_q for polymer-polymer reactions can also be converted to polymer self-diffusion coefficient, D , by using Eq. (3) together with $\gamma=0.61$ (HORIE 1978) for the present system.

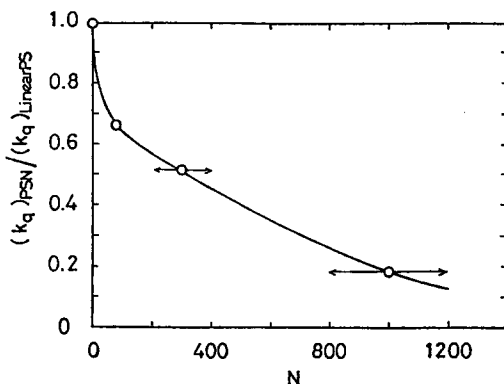


Fig. 3. Effect of chemical crosslinking for k_q at $C=0.18$ kg/dm³ against N of diffusing molecule

The self-diffusion coefficient for polystyrene with $N=10^3$ and $C=0.18$ kg/dm³ in benzene is reduced to one-fifth, when the surrounding polymer is moderately crosslinked with 2% divinylbenzene (PSN45). From diffusion experiments (data obtained by laser light-scattering spectroscopy and interpreted in terms of the sca-

ling theory - ADAM et al 1977) the number of monomer units between entanglement points, g , may be estimated: for $c = 0.18 \text{ kg/dm}^3$, 27 units have been found (if $N > 300$). This would suggest that the influence of chemical crosslinks on the molecular diffusion of linear polymers is much larger than the influence of physical entanglements in semidilute region.

In conclusion, the diffusion and collision rates of small molecules in semidilute polymer solution are not affected by the crosslink formation between polymer chains. However, the diffusion and diffusion-controlled reaction rates of end-labeled polymers in semidilute region are influenced much by the formation of chemical crosslinks between the inert polymer chains.

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