

Figure 3 Quenching of carbazole fluorescence by TCNE in methylene chloride at 298 K. ● I_0/I , ■ τ_0/τ both for carbazole 1.6×10^{-4} M; ○ τ_0/τ , □ I_0/I both for carbazole 8×10^{-4} M.

Quenching of fluorescence of carbazole by tetracyanoethylene in methylene chloride is illustrated in Figure 3. The lifetimes were measured using apparatus described previously¹. In this case there is no detectable difference between steady state intensity and lifetime data. In quantitative terms this means that less than ten percent of the carbazole is complexed at these concentrations so that the complexing equilibrium constant is less than $9(\text{M}^{-1})$. Data for 9-ethyl carbazole are similar, and so agree with literature values³⁻⁵ which range between 2 and 7.

Quenching of fluorescence of poly(9-carbazolyl methyl methacrylate) by tetracyanoethylene is illustrated in Figure 4. The quenching efficiency (slope of the τ_0/τ plot) is about a factor of two greater than for the small molecules (carbazole and 9-ethyl carbazole). There is also a marked difference between the lifetime (τ_0/τ) and steady state intensity (I_0/I) data. Analysis of this difference using equations 2 and 3 yields $K = 45.7$. This differs from literature reports which, using absorption in *much* more concentrated solutions, suggest that the complexing constant is *smaller* for polymers than for small molecules.

Similar measurements on collisional quenching by hexachlorobenzene produce coincidence of τ_0/τ and I_0/I Stern-Volmer plots as expected, again with quenching efficiencies about twice those observed for the small molecules.

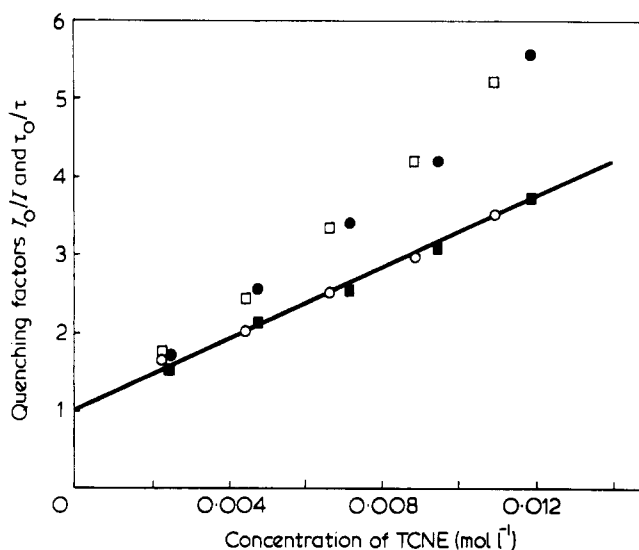


Figure 4 Quenching of polymer II 380 nm fluorescence by TCNE in methylene chloride at 298 K. ● I_0/I , ■ τ_0/τ both for 4.4×10^{-5} M monomer units; ○ τ_0/τ , □ I_0/I both for 8.8×10^{-5} M monomer units.

There are two possible explanations. The first is that in this polymer with the carbazolyl chromophore spaced away from the backbone, steric barriers to complex formation are eased, and of course, the entropy of complex formation will be less unfavourable with a polymeric substrate, so that K is genuinely larger than for small molecules. Alternatively, if K is similar to that observed for small molecules, each acceptor interacts with energy initially localized on about 8-9 donor chromophores. This might be by way of very limited excimer migration (2 or 3 'hops') or by rapid dissociation - reformation of the acceptor - donor complex so that 8 or 9 donor chromophores may complex with a single acceptor; indeed the complex may have a D_nA stoichiometry.

Studies on these questions are continuing.

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Entanglement effects in the segmental motion of two flexible chain polymers

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When the concentration of a dilute polymer solution is increased, interchain interactions occur first by hydrodynamic forces transmitted by intervening solvent mole-

cules, and then by direct intersegment interactions. When this interaction has sufficient strength and lasts sufficiently long to reduce the motional freedom of the participating

Table 1 Relaxation frequencies (GHz) of Poly(chloroprene) in toluene

Concentration % w/v	Viscosity poise at 273 K	223 K	273 K	298 K
5	0.4	1.1 ± 0.4	1.5 ± 0.5	1.9 ± 0.5
10	4.0	0.7 ± 0.2	0.8 ± 0.3	1.1 ± 0.3
20	42	0.5 ± 0.2	0.8 ± 0.1	1.1 ± 0.1

Table 2 Dielectric relaxation frequencies of poly(2,6-dimethyl 1,4-phenylene oxide) solutions 5% w/v containing added polystyrene, 323 K

Polystyrene concentration % w/v	Relaxation frequency MHz	Segment dipole moment <i>D</i>
0	8 ± 2	1.1
5	4 ± 1	0.68
15	0.7 ± 0.2	0.32
25	0.3 ± 0.1	0.35

chain sections it is referred to as an 'entanglement'. We have been interested in the ways that such chain entanglements affect both the long wavelength motions (normal modes) and the more localized (segmental) motions of dissolved molecules, and have completed ultrasonic relaxation studies of polystyrene¹ and poly(dimethyl siloxane)^{2,3} in which entanglements were created by increasing the concentration and the molecular weight of the polymer. These acoustic studies were most informative on the normal mode dynamics, and so in an analogous study we report here some observations of dielectric relaxation in solutions of poly(2,6 dimethyl 1,4 phenylene oxide) and poly(chloroprene). For these polymers the dielectric experiment observes orientation of the dipole component perpendicular to the chain contour⁴, and so probes the high frequency localized or segmental rotational motion.

Polymers derived from 1,3-dienes are often elastomeric, indicating that the chain flexibility is high, and we were concerned to determine whether entanglement effects would be less evident (because of the ease of segmental rotation) or more evident (because of the ability to form a geometrical knot) in such chains. Poly(2,6-dimethyl 1,4-phenylene oxide) in toluene is miscible with polystyrene. Since the former polymer is the more polar and dielectrically active we hoped to study entanglements introduced by the less polar and dielectrically inactive polystyrene at a constant concentration of the polyether.

The poly(chloroprene), Neoprene W from DuPont de Nemours, had \bar{M}_w of 5.3×10^5 and \bar{M}_n 7.2×10^4 . The poly(2,6 dimethyl 1,4 phenylene oxide) from General Electric Company had \bar{M}_w of 7.7×10^4 , \bar{M}_n 2.1×10^4 . The polystyrene had \bar{M}_w 1.2×10^5 and \bar{M}_n 3.7×10^4 . All solutions were in toluene and electrical measurements were made using the slotted line technique⁵ and transformer ratio arm bridges.

The relaxation frequencies, at three temperatures, of poly(chloroprene) solutions are listed in *Table 1*.

In none of the cases is there a reduction in relaxation frequency greater than the experimental error, which is particularly large in the most dilute solutions due to the inherent difficulty of the slotted line method and the corrections necessary in data handling⁵. The conclusion is, therefore, that the size of the rotating unit, or the distance over which there is correlation in the rotation of individual segments is less than the distance between entanglement points: or that the entanglement lifetime is less than the fraction of a nanosecond involved in segmental rotation. The authors prefer the former explanation, since the viscosity data clearly show the restricting effects of entanglements on longer wavelength slower motions. Such observations have importance in the consideration of theories which introduce the concept of a correlation, or correlation length, into the consideration of short wavelength chain motions.

Dielectric relaxation frequencies of toluene solutions of poly(2,6-dimethyl 1,4-phenylene oxide) containing various amounts of added polystyrene are listed in *Table 2*. Also listed are the apparent segment dipole moments calculated from the static permittivities using the Onsager relationship.

While it is immediately apparent that addition of polystyrene reduces the rate of chain segmental motion, the dipole moments show that unfortunately this is not due to simple entanglement of chains which are unaltered in all other respects. The thermodynamic interaction between the two polymers markedly alters the equilibrium conformation of the polyether chain, and the reduced mobility could be caused by this as much as by simple geometrical entanglement.

In summary, measurements of segmental mobility in solutions of polychloroprene show that very facile high frequency motions are little affected by the chain entanglements created in moderately concentrated solutions. Observations of segmental motion affected by addition of a second polymer are ambiguous since the phenomena observed may be due to structural changes as much as by simple entanglements.

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