(12) A. J. Roberts, D. Phillips, F. A. M. Abdul-Rasoul, and A. Ledwith, *J. Chem. Soc., Faraday Trans. 1*, **77**, 2725 (1981).
(13) I. Soutar, D. Phillips, A. J. Roberts, and G. Rumbles, *J. Polym. Sci., Polym. Phys. Ed.*, **20**, 1759 (1982).
(14) J. R. MacCallum, in "Photophysics of Synthetic Polymers", D. Phillips and A. J. Roberts, Eds., Science Reviews Ltd., Northwood, 1982.
(15) F. Schneider, *Z. Naturforsch., A*, **24a**, 863 (1969).
(16) C. David, D. Baeyens-Volant, and G. Geuskens, *Eur. Polym. J.*, **12**, 71 (1974).
(17) I. McInally, R. F. Reid, H. Rutherford, and I. Soutar, *Eur. Polym. J.*, **15**, 725 (1979).
(18) R. F. Reid and I. Soutar, *J. Polym. Sci., Polym. Phys. Ed.*, **16**, 231 (1978).
(19) R. F. Reid and I. Soutar, *J. Polym. Sci., Polym. Phys. Ed.*, **18**, 457 (1980).
(20) D. Phillips, A. J. Roberts, and I. Soutar, *J. Polym. Sci., Polym. Phys. Ed.*, **18**, 2401 (1980).
(21) D. Phillips, A. J. Roberts, and I. Soutar, *Polymer*, **22**, 293 (1981).

# Transient Decay Studies of Photophysical Processes in Aromatic Polymers. 7. Studies of the Molecular Weight Dependence of Intramolecular Excimer Formation in Polystyrene and Styrene–Butadiene Block Copolymers

**D. Phillips,[*,†] A. J. Roberts,[†] G. Rumbles,[†] and I. Soutar[*,‡]**

*The Davy-Faraday Research Laboratory, The Royal Institution, London W1X 4BS, United Kingdom, and Chemistry Department, Heriot-Watt University, Riccarton, Currie, Edinburgh EH14 4AS, United Kingdom.* *Received November 23, 1982*

ABSTRACT: A series of styrene homopolymers and styrene–butadiene block copolymers of type SB and SBSB in which the sequence length of styrene chromophores has been varied has been studied by time-resolved fluorescence techniques. It has been shown that the kinetic behavior of polystyrene fluorescence cannot be attributed to the existence of kinetically distinct monomeric species. The dual-exponential decays observed in the region of monomer emission are assigned to the influence of quenched monomer and excimer dissociation, respectively. The molar mass dependence of the polystyrene photophysics is best explained by models that assume energy migration to occur within (and, at low molecular weights, to be limited by) the chromophore sequence lengths.

## Introduction

While there has been an increased recognition that the photophysical behavior of macromolecules is not, in general, conducive for analogous small-molecule systems, the complex microheterogeneity of polymers has hindered agreement upon interpretation of the resultant kinetic data. In general, it is to be anticipated that the transient decay kinetics will require adoption of several decay coefficients for adequate description. The various models that have been proposed[1-7] differ principally in the identification of photophysical sites that are responsible for the dominant averages observed in the kinetic behavior. More fundamental question arise regarding the role and existence of energy migration in excimer formation. The subject has been recently reviewed.[8]

The decay kinetics of fluid solutions of polystyrene are less complex than those exhibited by other vinyl aromatic polymers[1,2] since the decay of excited monomer may be described in terms of a dual-exponential function.[9,10] As the heterogeneity of the chain microcomposition is increased through incorporation of randomly distributed spectroscopically inactive comonomer at varying intramolecular concentrations, the decay kinetics become more complex. This latter fact establishes credibility for mechanisms that impute[1-3] the involvement of excited-state monomeric entities that display a degree of isolation within the kinetic scheme relative to excited monomer subject to enhanced quenching through excimer formation. The absence of geometric isolation in polystyrene and the consequent simplification of the kinetics facilitate investigations of the factors governing excimer formation and testing of the validity of proposals regarding the nature of the excitation sites.

In previous reports we have shown that the intramolecular concentration dependence of excimer formation in certain polymers may be adequately described in terms of functions that incorporate terms descriptive of both energy migration and potential excimer site concentration.[1,2,9,11,12] In the case of one such function, involving mean chromophore sequence length and fraction of pairs of aromatic units, it has been suggested that energy migration need not be invoked in its derivation.[6,7] The alternative derivation implies differential photophysical activity between units that are centered in chromophoric sequences and those situated at the end of chromophoric blocks. Similar reasoning has been employed[6] to explain the observed molar mass dependence of the degree of excimer formation[13] in polystyrene.

In this paper we report investigations of the transient photophysical behavior of "monodisperse" polystyrene of varying molar mass and block styrene–butadiene copolymers of varying chromophore sequence length of both the type SB, containing a single block of styrene units, and the type SBSB, containing two styrene blocks. The results are pertinent to considerations of (1) the nature of the molecular weight dependence of excimer formation in polystyrenes, (2) the role of energy migration within blocks of chromophores in the excimer formation mechanism, (3) the question of distinctly different photophysical activity at sequence termini relative to chromophores situated within blocks, and (4) the extent to which long-range excimer interactions may occur as a result of either intrachain segmental or energy diffusion between blocks in copolymers containing more than one chromophoric sequence length. It has been inferred that the latter mechanism is of little significance in macromolecular

---

[†] The Royal Institution.

[‡] Heriot-Watt University.

0024-9297/83/2216-1597$01.50/0 © 1983 American Chemical Society

photophysics through studies of diblock copolymers,[14] head-to-head polystyrene,[14,15] and molar mass independence of quenching efficiency[15] under steady-state excitation. However, transient excitation experiments under conditions of high signal-to-noise ratio will be sensitive to deviations from "ideal" kinetic behavior that might result from minor deactivation pathways and thus will provide a more regorous test of the occurrence of long-range influences upon excimer formation than has previously provide possible.

## Experimental Section

**Methods.** Fluorescence decay data were obtained by the single-photon-counting technique on a high-resolution spectrometer in which excitation at 257.3 nm was achieved by using the frequency-doubled, cavity-dumped output of a 4-W argon ion laser (Spectra-Physics Model 166). Details of the spectrometer have been previously described.[10] Decay data were collected to a minimum of $3 \times 10^4$ counts in the channel of maximum population. The "goodness of fit" criteria employed in this work have been described elsewhere.[16]

**Materials.** Styrene–butadiene, SB and SBSB, block copolymers were prepared by "living polymer" synthetic methods as previously described.[14] Butadiene polymerization was initiated in dry benzene by butyllithium in the presence of a small amount of THF. Styrene was added to the living polymer in such quantity as to produce aromatic sequences of the desired length. Subsequent addition of butadiene and styrene produced BSBS block copolymers.

Polystyrenes prepared by the living polymer technique were synthesized in a similar manner to the block copolymers.

Dichloromethane (BDH) was purified by fractional distillation and checked for purity by fluorescence spectroscopy.

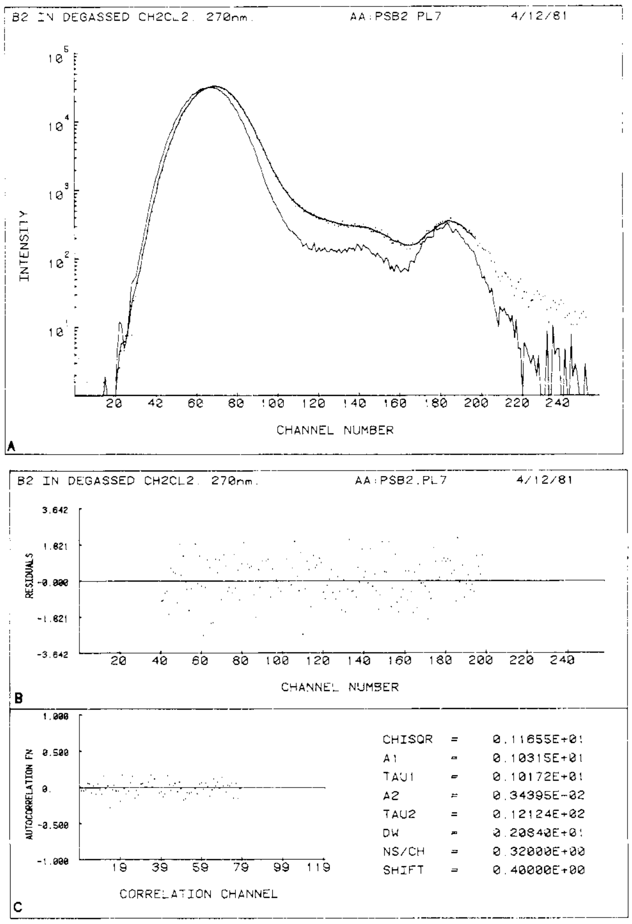
Fluorescence spectra were recorded on thoroughly degassed dichloromethane solutions of optical density 0.1.

## Results and Discussion

**Analysis Procedure.** Fluorescence decay curves were recorded in the region of monomer emission at 270 nm. The monomer decay curve $i_m(t)$ could not be satisfactorily described as a single-exponential decay for any of the samples analyzed. The decays were well characterized for all polymers [as judged by reduced $\chi^2$ (<1.3), weighted residuals, autocorrelation function, and Durbin and Watson parameter (>1.75) as discussed elsewhere[16]] by dual-exponential functions of the form

$$i_m(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2) \qquad (1)$$

Figure 1 shows a typical decay (sample B2, styrene–butadiene copolymer, $N_S = 21$) and residuals and autocorrelation of residuals for single- and dual-exponential fits. The applicability of dual-exponential fits in the description of the decay of $i_m(t)$ is consistent with our previous experience[10] in the photophysical characterization of free radically initiated styrene homopolymers. The ability of dual-exponential functions to describe the decay data over the whole range of chromophore block lengths is significant in that there is no evidence in these data for the presence of a kinetically isolated monomer as postulated[1,2,12] in explanation in triple-exponential fitting of polymers containing naphthyl chromophores. Moreover, the suitability of the dual-exponential analysis implies an independence of decay behavior upon the location of chromophoric groups at terminal or internal situations within the styrene blocks. This observation is elaborated upon at a later stage in this paper.



```
CHISQR   =    0.11655E+01
A1       =    0.10315E+01
TAU1     =    0.10172E+01
A2       =    0.34395E-02
TAU2     =    0.12124E+02
DW       =    0.20840E+01
NS/CH    =    0.32000E+00
SHIFT    =    0.40000E+00
```

**Figure 1.** Typical fluorescence decay curve and analysis for sample $B_2$: (A) plot of experimental decay curve (points) and computed best fit to eq 1 (line); (B) plot of weighted residuals; (C) autocorrelation function. (One channel ≡ 0.32 ns.)

Dual-exponential fitting to the decay data considerably simplifies the mathematical analysis of the transient photophysical behavior of these styrene-containing systems relative to those containing, e.g., naphthalene chromophores. The mathematical treatment of the data reduces to a form analogous to that predicted by the Birks[17] treatment in low molar mass media. Consequently, using Birks nomenclature,[17] the rates of monomer and excimer formation are given by eq 2 and 3, respectively, as

$$d[M^*]/dt = I_a(t) + k_{MD}[D^*] - X[M^*] \qquad (2)$$

and

$$d[D^*]/dt = k_{DM}[M][M^*] - Y[D^*] \qquad (3)$$

where

$$X = k_M + k_{DM}[M] \qquad (4)$$

and

$$Y = k_D + k_{MD} \qquad (5)$$

For $\gamma$-function excitation a dual-exponential decay function for $i_m(t)$ results of the form of eq 1, where

$$\tau_{1,2}^{-1} = \lambda_{1,2} = \tfrac{1}{2}[(X + Y) \mp \{(X - Y)^2 + 4k_{MD}k_{DM}[M]\}^{1/2}] \qquad (6)$$

$$\lambda_1 + \lambda_2 = k_M + k_{DM}[M] + k_{MD} + k_D \qquad (7)$$

and

$$\lambda_1\lambda_2 = k_M(k_D + k_{MD}) + k_Dk_{DM}[M] \qquad (8)$$

As has been discussed previously,[1,3] the concentration term [M] describes a finite but unknown intramolecular chromophore concentration. Given the applicability of the kinetic scheme described above, individual rate parameters in the kinetic scheme may be determined by successive application of the following kinetic relations:

$$X = (B\lambda_2 + \lambda_1)/(B + 1) \qquad (9)$$

Table I
Kinetic Parameters for Polystyrene Homopolymers and Copolymers

| sample[a] | $N_S$[b] | $A_1$ | $\tau_1$/ns | $A_2$ | $\tau_2$/ns | $k_{DM}[M]/10^7\ s^{-1}$ | $k_D/10^7\ s^{-1}$ | $k_{MD}/10^7\ s^{-1}$ |
|---|---|---|---|---|---|---|---|---|
| H1 | 15 | 0.93 | 1.09 | 0.044 | 10.13 | 83.9 | 10.1 | 3.4 |
| H2 | 16 | 0.50 | 1.14 | 0.004 | 11.07 | 83.6 | 9.1 | 0.6 |
| H3 | 17 | 1.03 | 0.89 | 0.015 | 14.73 | 106.5 | 6.8 | 1.5 |
| H4 | 23 | 1.21 | 0.84 | 0.006 | 11.77 | 115.2 | 8.5 | 0.5 |
| H5 | 27 | 1.04 | 0.81 | 0.011 | 14.14 | 118.8 | 7.1 | 1.2 |
| H6 | 168 | 1.44 | 0.68 | 0.011 | 13.22 | 142.7 | 7.6 | 1.0 |
| H7 | 1060 | 1.40 | 0.72 | 0.004 | 13.54 | 135.0 | 7.4 | 0.4 |
| B1 | 16 | 0.79 | 1.34 | 0.003 | 11.68 | 70.7 | 8.6 | 0.2 |
| B2 | 21 | 1.03 | 1.02 | 0.003 | 12.12 | 94.1 | 8.3 | 0.3 |
| B3 | 40 | 0.86 | 0.80 | 0.002 | 13.91 | 120.4 | 7.2 | 0.2 |
| B4 | 82 | 1.49 | 0.81 | 0.014 | 11.28 | 118.5 | 8.9 | 1.0 |
| D1 | 6 | 0.53 | 1.51 | 0.057 | 11.49 | 56.7 | 9.2 | 5.1 |
| D2 | 9.5 | 0.81 | 1.19 | 0.009 | 11.65 | 79.1 | 8.6 | 0.7 |
| D3 | 21 | 1.07 | 1.00 | 0.030 | 11.84 | 93.3 | 8.6 | 2.4 |
| D4 | 25 | 0.84 | 0.96 | 0.050 | 11.47 | 95.4 | 9.0 | 5.1 |
| D5 | 45 | 1.25 | 0.81 | 0.021 | 14.57 | 118.1 | 6.9 | 1.9 |
| D6 | 96 | 1.26 | 0.77 | 0.008 | 12.53 | 125.5 | 8.0 | 0.8 |

[a] H refers to homopolymers, B to single block copolymers of the type SB and D to block copolymers of the type SBSB.
[b] Number of styrene units in the sequence length. Values listed for D1-D6 are the arithmetic means of the two individual sequence lengths.

where $B = A_2/A_1$, $A_1$ and $A_2$ being the preexponential terms defined in eq 1,

$$k_{DM}[M] = X - k_M \qquad (10)$$

$$Y = \lambda_1 + \lambda_2 - X \qquad (11)$$

$$k_{MD} = \frac{(X - \lambda_1)(\lambda_2 - X)}{k_{DM}[M]} \qquad (12)$$

and

$$k_D = Y - k_{MD} \qquad (13)$$

The resultant rate parameters are detailed in Table I along with the "raw" kinetic data from eq 1 and compositional parameters defining the styrene lengths in the homopolymers, single (chromophore) block copolymers, and dual (chromophore) block copolymers.

**Molar Mass Dependence of Rate Parameters.** Reference to the data presented in Table I reveals that the rate coefficients for excimer deactivation by dissociation to monomer, $k_{MD}$, and by all other photophysical means, $k_D$, are (within the considerable errors incurred in the analysis) independent of chromophore sequence length. The relatively large errors in derivation of $k_{MD}$ and $k_D$ are the result of successive application of eq 10–13 and consequent error accumulation. In particular, it should be noted that the value of $k_M$ applied in eq 10 is that obtained by extrapolation to negligible styrene composition in a series of random styrene/methyl methacrylate copolymers[9] and that derivation of $k_{MD}$ in eq 12 involves the use of empirical data based upon four freely varied fitting parameters $A_1$, $A_2$, $\lambda_1$, and $\lambda_2$ as defined in eq 1 and a subsequently derived quantity $X$, which upon combination with the value of $k_M$ yields $k_{DM}[M]$. Consequently, we are unable to comment upon the molar mass dependence of $k_{MD}$ and therefore cannot quantify the importance of decreased dissociation of excimer at higher molar mass described by Ishii et al.[13] In the latter case the rate constants of excimer formation and dissociation were derived from steady-state expressions for fluorescence of excimer and monomer allied to quenching rate data.

Figure 2 shows the dependence of the term $k_{DM}[M]$ upon the number of styrene-derived chromophores in a continuous sequence length in the homopolymer, single block copolymer, and dual block copolymer systems. A smooth curve, concave to the molar mass axis, is produced, provided the data obtained for the copolymers containing two styrene sequence lengths are calculated assuming negligible interaction between the separate chromophoric blocks. The general trend in the data compares well with that reported by Ishii et al.[13] for the rate constant for excimer formation in polystyrene homopolymers and those reported for steady-state excimer to monomer ratios[13-15] as a function of styrene sequence length.

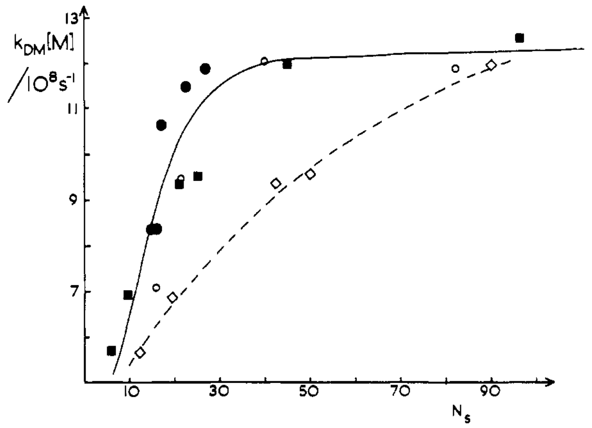


**Figure 2.** Plot of $k_{DM}[M]$ vs. $N_S$: (●) homopolymers; (○) block copolymers of type SB; (■) double block copolymers of type SBSB; (◇) double block copolymers, plotted with $N_S$ reprsenting the *total* number of styrene units in the polymer.

The superposition of dual block excimer formation rate data upon those of the homopolymers and single-block species under these conditions emphasizes the negligible influence of long-range interactions (whether of a diffusive or energy-transfer nature) upon the photophysical behavior. Indeed the lack of involvement of long-range interactions is reinforced by the distinct incompatibility of the dual block copolymer data when the overall styrene composition is considered (cf. Figure 2). The evidence for such a conclusion derived from steady-state excitation data has been discussed previously.[18]

In conclusion it should be stressed that the sensitivity of the fitting criteria (as applied to dual-exponential fits) under transient excitation conditions with the high signal-to-noise ratios characteristic of the experiments performed in this work would have detected deviations other than those of negligible significance, which might have resulted from either (a) long-range interactions effecting juxtaposition of chromophores through the agency of large-scale motion of polymer segments distant on the polymer chain or (b) energy transfer (e.g., by a Förster mechanism) between in the SBSB copolymers.

**Interpretation of Photophysical Data.** The derived decay parameters and their molecular weight dependence discussed in the previous section allow firm conclusions to be reached regarding the nature of the kinetic sites and their mutual interactions.

The kinetic treatment outlined above has assumed that the dual decay parameter combination of $\lambda_{1,2}$ results from the existence of one excited monomeric species that is capable of interacting to form an excimeric state. In this scheme the longer decay time is consequent upon feedback to excited monomer through excimer dissociation. In this respect the data analysis is consistent with our previous results upon styrene-containing polymers and random copolymers.[9,10,19]

The alternative interpretation which would be implied by the suggestions of MacCallum[6,7] that kinetic discrimination is resultant upon differences in compositional environment within the chain may be discounted as discussed below. According to these arguments the dual-exponential decay in the region of monomer emission would be ascribable to the decay of excited styryl units located in environments of the type $-S\overset{*}{S}S-$ and $-B\overset{*}{S}S-$ i.e., at sequence interiors and termini, respectively. Furthermore, it is assumed that excimer dissociation to excited monomer does not occur.[7] This model is not consistent with the observed photophysical behavior for the following reasons.

(1) Intuitively, it could be reasoned that if the differences in kinetic activity of $-S\overset{*}{S}S-$ and $-B\overset{*}{S}S-$ are solely the result of reduced probability of excimer formation as a consequence of the 2:1 ratio of potential excimer sites (and modification of rotational mobility by differences in geometric constraints in the two triad situations), the ratio of the two decay times would be much greater than observed. In other words, it would be expected to a first approximation that given a value of ca. 1 ns for $\tau_1$ descriptive of $-S\overset{*}{S}S-$ decay, $\tau_2$ for $-B\overset{*}{S}S-$ triads would be expected to have a value in the region of 2–3 ns (provided $k_M < k_{DM}$). Reference to the decay data of Table I for these block copolymers or those reported for homopolymers(9) and random styrene copolymers[7,9] reveals that $\tau_2$ in all instances is much greater than $\tau_1$ and of the order of magnitude observed for that of excimer from decay analysis in the spectral region of excimer emission.

(2) Recent work[19,20] in which the emission of styrene sequences was quenced by intramolecular energy acceptors has shown that not only do two decay rates exist in such a situation but that the long-lived emission is unquenched. These observations would not be anticipated from the MacCallum[6,7] model since the ends of sequence styrene chromophores are located adjacent to the energy traps. Consequently, regardless of the mechanism of energy quenching the terminal groups should be subject to severe quenching as a result of considerations of distance and long unquenched lifetime.

(3) The qualitative reasoning presented in (1) and (2) above may be reinforced by the following quantitative assessment of the model. If $\tau_1$ and $\tau_2$ are associated with excited states of the type $-S\overset{*}{S}S-$ and $-S\overset{*}{S}B-$, respectively, then the relative contributions to the decay profiles, $A_1\tau_1/A_2\tau_2$, should be directly proportional to the ratio of the number of styrene chromophores situated in $-SSS-$ triads to that in $-BSS-$ triads. The data are presented in Figure 3. It is apparent that the relation between $A_1\tau_1/A_2\tau_2$ and $N_{SSS}/N_{SSB}$ is characterized by an extremely low degree of correlation. Consequently, we have no evidence for the kinetic discrimination between excited monomeric sites in styrene polymers which might be induced by differences in location within the chain.

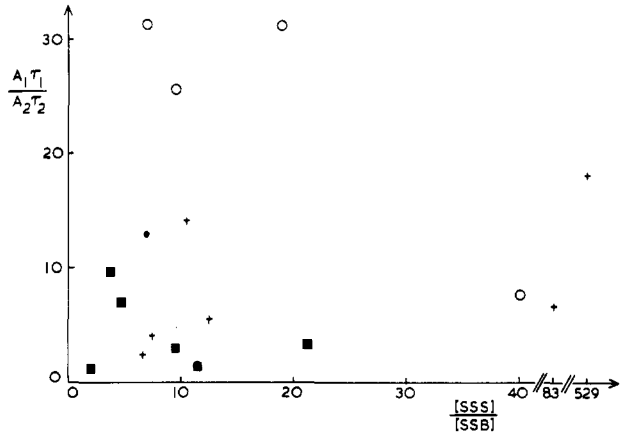


**Figure 3.** Plot of relative contributions of component 1 to component 2 vs. ratio of mid groups to end groups in the polymer.

To summarize, we believe that the dual-exponential decays obtained in the region of monomer emission in styrene polymers are not the result of the existence of two excited-state monomeric species distinguished by microcompositional difference but rather a consequence of the existence of two monomeric excited states separated in lifetime through their mode of creation: One state occurs as a result of energy absorption and is quenched by excimer formation. The other excited state is formed upon dissociation of the excimer.[9,10] Both $\tau$ values are averaged quantities representative of the total assemblage of excited-state chromophores within the system.

**Consolidation.** Following the above discussion it is possible to reconsider the nature of the molar mass dependence of excimer formation in polystyrene.

Reference to Figure 2 reveals that there are two distinct kinetic regimes. Below ca. 25 styrene units, $k_{DM}[M]$ increases in an almost linear fashion with increasing styrene content. Above ca. 35 styrene units, the function $k_{DM}[M]$ becomes independent of molar mass. Since we have shown that the results are inconsistent with the existence of two kinetically distinct excited monomeric species in these block copolymers, it is difficult to explain the form of the molecular weight dependence without invoking the concept of energy migration.

The function $k_{DM}[M]$ is a composite term comprising a rate coefficient $k_{DM}$ that wil reflect contributions from exciton migration and micro-Brownian rotational motions of the chromophoric groups. The concentration term [M] represents the distribution of potential excimer sites within the diffusion length of the exciton. In the low molecular weight range the exciton path length is defined by the chromophore block length and consequently the kinetic behavior is determined by the concentration of potential excimer sites within the block. The probability of enerby trapping by an excimeric site is dictated by the probability of excimer site creation, which, in turn, depends upon the number of chromophore pairs within the block length. Consequently, $k_{DM}[M]$ increases with styrene sequence length.

In the high molecular weight region $k_{DM}[M]$ tends to a constant value, which is indicative that once the styrene sequence length exceeds ca. 35, the probability of energy population of an excimer site is no longer dictated by the number of chromophoric pairs. This implies that the energy is delocalized over an average about 35 styrene units and is limited to this extent by energy trapping at excimer sites. Similar considerations will apply to the dependence of $I_D/I_M$ upon molecular weight studied in steady-state excitation.[13-15]

## Conclusions

The studies described in this paper have led to the following conclusions.

(1) There is no justification for the proposal[6,7] that excited monomeric styrene residues may be kinetically distinguishable as a consequence of their location within -SSS- as opposed to -SSB- triads.

(2) The kinetics of intramolecular excimer formation in polystyrenes show a molecular weight dependence that is characterized by two distinct regions. This behavior is best explained by implication of energy migration within chromophore sequences.

(3) In agreement with conclusions from steady-state excitation analyses,[14,18] there is no evidence for long-range interactions in excimer formation in polystyrenes.

**Acknowledgment.** Financial support from the Science and Engineering Research Council, Royal Society, Nuffield Foundation, and the U.S. Army European Research Office is gratefully acknowledged. G.R. acknowledges receipt of an SERC CASE studentship in collaboration with ICI Corporate Laboratory, Runcorn, UK.

**Registry No.** Styrene/butadiene copolymer, 9003-55-8; polystyrene, 9003-53-6.

## References and Notes

(1) D. Phillips, A. J. Roberts, and I. Soutar, *J. Polym. Sci., Polym. Phys. Ed.*, 18, 2401 (1980).
(2) D. Phillips, A. J. *Roberts*, and I. Soutar, *J. Polym. Sci., Polym. Phys. Ed.*, **20**, 411 (1982).
(3) D. A. Holden, P. Y.-K. Wang, and J. E. Guillet, *Macromolecules, 13*, 295 (1980).
(4) F. C. De Schryver, D. Demeyer, M. Van der Auweraer, and E. Quanten, Ann. N.Y. Acad. Sci., **366**, 93 (1981).
(5) K. Demeyer, M. Van der Auweraer, L. Aerts, and F. C. De Schryver, *J. Chim. Phys.*, **77**, 493 (1980).
(6) J. R. MacCallum, *Eur. Polym. J.*, **17**, 797 (1981).
(7) J. R. MacCallum, in "Photophysics in Synthetic Polymers", D. Phillips and A. J. Roberts, Eds., Science Reviews Ltd., Northwood, 1982.
(8) A. J. Roberts and I. Soutar, in "Photoluminescence in Synthetic Polymers", D. Phillips, Ed. Chapman and Hall, London, in press.
(9) I. Soutar, D. Phillips, A. J. Roberts, and G. Rumbles, *J. Polym. Sci., Polym. Phys. Ed.*, in press.
(10) G. Rumbles, in "Photophysics in Synthetic Polymers", D. Phillips and A. J. Roberts, Eds.; Science Reviews Ltd., Northwood, 1982.
(11) R. F. Reid and I. Soutar, *J. Polym. Sci., Polym. Phys. Ed.*, **16**, 231 (1978).
(12) D. Phillips, A. J. Roberts, and I. Soutar, *Eur. Polym. J.*, **17**, 101 (1981).
(13) T. Ishii, T. Handa, and S. Matsunaga, *Macromolecules*, 11, 40 (1978).
(14) W. E. Lindsell, F. C. Robertson, and I. Soutar, *Eur. Polym. J.*, 17, 203 (1981).
(15) J. M. Torkelson, S. Lipsky, and M. Tirrell, *Macromolecules*, **14**, 1603 (1981).
(16) A. J. Roberts, D. Phillips, F. A. M. Abdul-Rasoul, and A. Ledwith, *J. Chem. Soc., Faraday Trans. 1*, **77**, 2725 (1981).
(17) J. B. Birks, "Photophysics of Aromatic Molecules", Wiley, New York, 1970.
(18) I. Soutar, *Ann. N.Y. Acad. Sci.*, **366**, 24 (1981).
(19) D. Phillips, A. J. Roberts, and I. Soutar, *Macromolecules*, preceding paper in this issue.
(20) A. J. Roberts, in "Photophysics in Synthetic Polymers", D. Phillips and A. J. Roberts, Eds.; Science Reviews Ltd., Northwood, 1982.

---

# Theory of Strain Birefringence of Amorphous Polymer Networks

**Burak Erman[†] and Paul J. Flory***

*IBM Research Laboratory, San Jose, California 95193.* *Received February 24, 1983*

ABSTRACT: Recent rubber elasticity theory, according to which departures from relationships derived for phantom networks originate in constraints on the fluctuations of network junctions, is applied to the treatment of strain birefringence. The strain birefringence of phantom networks is first considered. It is smaller than for networks in which the transformation of chain vectors is affine in the macroscopic strain, as assumed in all previous treatments of strain birefringence in rubber elastic systems. The relationship of birefringence to the stress is the same, however. Real networks, in which the constraints on fluctuations impart a pattern of behavior intermediate between the extremes of phantom and affine networks, are treated in detail by extension of rubber elasticity theory. Illustrative numerical calculations are presented. Contributions of the constraints to the birefringence $\Delta n$ are somewhat larger, relatively, than their contributions to the stress $\tau$. In contrast to theories of phantom and of affine networks, $\Delta n$ for the real network is predicted to be nonlinear with $\tau$ for uniaxial extension; i.e., the stress-optical coefficient $\Delta n/\tau$ should decrease with elongation.

## Introduction

The birefringence of an amorphous polymer network under strain reflects the orientation of the structural units comprising the chains of the network. More precisely, it depends directly on the mean orientations of the optical polarizability tensors associated with the structural units.[1,2] Analysis of the strain-induced birefringence rests on establishment of connections between orientation at a molecular level and the macroscopic state of strain. Close parallels with molecular theories of rubber elasticity have long been recognized.[1,3,4]

Heretofore, the theory of strain birefringence of elastomeric polymer networks[1-6] has been formulated on the basis of the affine network model, according to which the transformation of the chain vectors (i.e., the vectors spanning the chains between network junctions) is linear in the macroscopic strain. This model has been discredited by recent investigations, both theoretical[7-10] and experimental.[1,11] The distribution of chain vectors that characterizes the system at a molecular level undergoes a

---

[†] Permanent address: School of Engineering, Bogazici University, Bebek, Istanbul, Turkey.