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Studies of the Electronic Energy Migration and Trapping in Styrene Copolymers

K. Sienicki* and C. Bojarski

Institute of Physics, Technical University of Gdańsk, 80-952 Gdańsk, Poland.

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ABSTRACT: Measurements of the quantum yields of monomer and excimer fluorescence of statistical styrene copolymers with methyl methacrylate, ethyl acrylate, and acrylonitrile were carried out in 1,2-dichloroethane. The experimental data were analyzed within the theoretical model, taking into account the existence of isolated and nonisolated chromophoric groups in a copolymer chain. The numbers of excimer-forming sites in these copolymers were determined, and it was shown that they are proportional to the fraction of linkages between styrenes. The process of self-quenching of monomer fluorescence in styrene copolymers was observed.

Introduction

The investigation of the processes of migration and transfer of electronic excitation energy in synthetic macromolecules is important both from the scientific and practical point of view. Among others, these processes play an important role in the photodegradation of macromolecules[1,2] and in the design of macromolecular antenna systems for efficient harvesting of solar energy.[3]

The main factor distinguishing macromolecules from small molecules is the fact that in a very dilute macromolecule solution an efficient process of excitation energy migration (EM) and excimer formation takes place.[4-7] It has been shown that the formation of excimers is preceded by the EM process, which is controlled by a number of factors related to the macromolecule structure.[8-14] In particular, the decrease of chromophoric group concentration by formation of copolymers allows a detailed analysis of the luminescence processes in macromolecules.[7,15a]

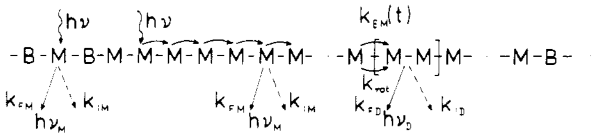
The pioneer research of David et al.[16] indicates that in styrene copolymers with methyl methacrylate (S-*co*-MMA) and methacrylate, excimer emission (I_D), relative to monomer emission (I_M), depends linearly (up to 70% of styrene in copolymer) on the concentration of potential excimer-forming sites, i.e., the styrene diad fraction (f_{MM}). The authors deduced that excimer formation in these copolymers is associated with energy migration. The later work of Reid and Soutar[17a] for S-*co*-MMA and 1-vinylnaphthalene and 2-vinylnaphthalene copolymers with methyl methacrylate also confirmed the conclusions of David et al. and showed that in these copolymers EM may be characterized in terms of the mean sequence length ($\bar{l}_M$) of aromatic species and that the concentration of excimer-forming sites (EFS) for these systems is proportional to the fraction of linkages between aromatic species.

In the work mentioned, it was assumed that EM is restricted to particular sequences in the copolymer. However, as was recently shown for certain copolymers,[2,17b,18] one must consider the possibility of EM between sequences. One must assume that this fact is particularly relevant for systems for which the Förster critical radius[19] is comparable with intrachain distances.

Lately MacCallum[20] has criticized the treatment of David et al.[16] and Reid and Soutar,[17] indicating that in their considerations the authors neglected the existence of isolated aromatic species, which does not contribute to the intensity of excimer fluorescence.

This paper contains investigations of quantum yields of statistical styrene copolymers with methyl methacrylate, ethyl acrylate, and acrylonitrile in solution. The experimental data were interpreted on the basis of a model considering the existence of isolated and nonisolated styrenes in the copolymer chain.

Scheme I



Model

We consider a statistical copolymer formed of two kinds of monomeric units, i.e., spectroscopically active (M) and inactive (B). As in the previous work,[15a] all sequences of active monomeric units have been divided into two groups: (a) sequences consisting of one monomeric unit; (b) all remaining sequences. The latter have been substituted by a sequence with mean length $\bar{l}_M$ (in monomeric unit lengths). This simplification enables the solution of a problem that becomes complicated when the distributions of sequences with different lengths must be taken into account. The photophysical processes illustrated in Scheme I have been assumed to occur: M–M stands for intramolecular excimer D and $(k_{FM} + k_{IM})^{-1} = \tau_{OM}$ and $(k_{FD} + k_{ID})^{-1} = \tau_{OD}$ are the monomer and excimer lifetimes in the excited state. We assume that excimers are formed as a result of two processes. The first is energy migration with a rate constant $k_{EM}(t)$, and the second is segmental rotation about a backbone bond with a rate constant k_{rot}. Excimers may also form as a result of direct absorption by prepared excimer sites (meso-tt conformations[7b]); however, due to their small concentration, this effect may be omitted in the first approximation.

Assuming that excimer dissociation is negligible, which is true for certain polymers,[4] the expressions for quantum yields of isolated ($\Phi_M^{(a)}$) and nonisolated ($\bar{\Phi}_M^{(b)}$) monomers and excimers (Φ_D) in the following form were obtained (see Appendix):

$$\Phi_M^{(a)} = Pk_{FM}\tau_{OM} \tag{1}$$

$$\bar{\Phi}_M^{(b)} = (1 - P)k_{FM}\tau_M[1 - f(\Gamma_M)] \tag{2}$$

$$\Phi_D = \frac{4\pi(1 - P)k_{FD}\bar{\Lambda}r_{DD}q}{\tau_M^{-1} - \tau_{OD}^{-1}}\Bigg\{1 + (\pi(\tau_M^{-1} - \tau_{OD}^{-1}))^{1/2}\exp(\Gamma_M^2/(1 - \tau_M/\tau_{OD})) \times \left[\frac{r_{DD}}{(\pi\bar{\Lambda})^{1/2}} - \frac{\Gamma_M}{\tau_M^{1/2}(\tau_M^{-1} - \tau_{OD}^{-1})}\right]\left[1 - \operatorname{erf}\left(\frac{\Gamma_M}{(1 - \tau_M/\tau_{OD})^{1/2}}\right)\right]\tau_{OD} - \tau_M[1 - f(\Gamma_M)]\Bigg\} \tag{3}$$

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Table I
Statistical Composition of Styrene Copolymers

sample	f_M/f_B	f_M	R	f_{MM}	$\bar{l}_M$	P
Comonomer: Methyl Methacrylate, $r_M = 0.58$, $r_B = 0.46$[17]						
1	0.005	0.011	2.138	0.000	2.003	0.996
2	0.064	0.126	21.681	0.017	2.037	0.930
3	0.150	0.209	38.807	0.015	2.087	0.846
4	0.553	0.405	63.440	0.088	2.321	0.573
5	0.818	0.485	65.859	0.156	2.474	0.460
6	1.232	0.565	64.768	0.241	2.715	0.340
7	1.710	0.620	61.335	0.313	2.992	0.252
8	4.155	0.758	44.242	0.537	4.410	0.086
9	6.811	0.830	33.218	0.664	5.952	0.041
10	12.333	0.885	21.762	0.776	9.153	0.015
11	28.420	0.945	10.811	0.891	18.484	0.003
12	∞	1.000	0.000	1.000	∞	0.000
Comonomer: Ethyl Acrylate, $r_M = 0.79$, $r_B = 0.15$[22]						
1	0.079	0.059	50.490	0.000	2.062	0.886
2	0.401	0.241	74.326	0.000	2.317	0.577
3	1.015	0.445	67.805	0.106	2.802	0.308
4	1.239	0.495	64.519	0.172	2.978	0.255
5	3.077	0.709	44.647	0.486	4.431	0.085
6	3.786	0.749	39.758	0.550	4.991	0.063
7	10.036	0.888	20.114	0.787	9.928	0.013
8	21.016	0.943	10.742	0.889	18.603	0.003
9	∞	1.000	0.000	1.000	∞	0.000
Comonomer: Acrylonitrile, $r_M = 0.37$, $r_B = 0.05$[23]						
1	0.821	0.468				0.730
2	1.501	0.600				0.360
3	3.127	0.758				0.075
4	6.123	0.860				0.015
5	21.220	0.955				0.005
6	49.112	0.980				0.001
7	∞	1.000				0.000

P is the probability of finding an isolated chromophore group in copolymer chain, $\bar{\Lambda}$ is the EM coefficient, r_{DD} is the capture radius of excitation by excimers, q is a concentration of excimer-forming sites (EFS), and

$$\tau_M^{-1} = \tau_{OM}^{-1} + (4\pi\bar{\Lambda}r_{DD} + k_{rot})q$$

$$\Gamma_M = 4(\pi\bar{\Lambda}\tau_M)^{1/2}r_{DD}^2q$$

$$f(\Gamma_M) = \pi^{1/2}\Gamma_M \exp(\Gamma_M^2)[1 - \text{erf}(\Gamma_M)]$$

Equations 1–3 will be helpful in the analysis of styrene copolymers quantum yields in the latter part of the paper.

Experimental Section

Styrene (S) (International Enzymes Ltd.), methyl methacrylate (MMA) (UCB-Bruxelles), ethyl acrylate (EA) (Fluka AG), and acrylonitrile (AN) (Fluka AG) were fractionally distilled before use. Statistical copolymers of S-*co*-MMA, S-*co*-EA, and S-*co*-AN were obtained by bulk polymerization at 343 K using 0.6% w/w α,α'-azobis(isobutyronitrile) (Fluka AG) initiator under a nitrogen atmosphere. Copolymers S-*co*-MMA and S-*co*-AN were purified by multiple reprecipitation (dissolving in 1,2-dichloroethane (DCE) and precipitation in methanol). Copolymers S-*co*-EA were precipitated in hexane. In each case the copolymers were held under high vacuum at 308 K for about 200 h. All solvents were purified by standard methods and tested before use for fluorescent impurities.

Copolymer composition was controlled by UV absorption (VSU2-P, Zeiss Jena) and NMR (Varian 360). Table I lists the copolymer microcomposition data necessary for description of the photophysical behavior of S-*co*-MMA, S-*co*-EA, and S-*co*-AN. Copolymerization parameters for S-*co*-MMA and S-*co*-EA were obtained from the terminal model[21] in the following way. The value of parameter f_{MM} (the fraction of linkages between styrene moieties in the copolymer chain) was calculated from the relation[21]

$$f_{MM} = f_M - R/200$$

with $R = 200/(2 + r_Mf_M/f_B + r_Bf_B/f_M)$, where R is the average number of continuous monomer sequences per hundred monomeric units, f_M and f_B are mole fractions of styrene and luminescently inactive comonomer, respectively, and r_M and r_B are reactivity ratios. (See Table I.) The probability P that a given styrene unit has the MMA or EA units on both left and right sides is given by[20]

$$P = [r_Mf_M/(f_B + 1)]^{-2}$$

The mean styrene sequence (for b type styrene units) length was calculated from the relation

$$\bar{l}_M = (2 + r_Mf_M)/f_B$$

In the case of S-*co*-AN, as has been recently shown,[23] one cannot apply the terminal model to the copolymerization process. That is why the probability P for S-*co*-AN was determined from the results obtained by Hill et al.[23] from their investigations of ^{13}C NMR.

Fluorescence measurements were carried out at room temperature in DCE, which before use was purified from Cl_2 and H_2O according to standard methods. (DCE and copolymers were stored in darkness.) Copolymer concentration in solutions was 2×10^{-3} mol·L^{-1} (in phenyl group units). The relative fluorescence quantum yields of the copolymers were determined from the area of the fluorescence spectra relative to the area of the spectra for ethyl benzene in deaerated cyclohexane, assuming that its quantum yield was 0.18.[24] Dissolved oxygen was removed by bubbling nitrogen gas through the sample solution in the cell. Fluorescence spectra were obtained by using apparatus described in ref 15b and were corrected for the wavelength dependence of the instrument response. Monomer and excimer bands were deconvoluted by using standard methods.[25,26]

Results and Discussion

Copolymers of S-*co*-MMA and S-*co*-EA. The experimental values of quantum yields of monomer (Φ_M) and excimer (Φ_D) fluorescence of copolymers S-*co*-MMA and S-*co*-EA as a function of the mole fraction of styrene (f_M) in a copolymer chain in DCE are shown in Figure 1, parts a and b. The theoretical curves representing quantum yields (broken and full lines) were determined on the basis of eq 1–3 for parameters compiled in Table I and for τ_{OM} = 13 ns,[27] τ_{OD} = 15.3 ns,[28] $k_{FM} = 6.85 \times 10^6$ s^{-1}, $k_{FD} = 8.44 \times 10^5$ s^{-1},[29] and r_{DD} = 6.5 Å. The value of k_{FM} was determined from the relation $\Phi_{EB} = k_{FM}\tau_{OM}$, where Φ_{EB} = 0.089. The value of Φ_{EB} was determined for ethylbenzene (EB) in DCE on an apparatus the details of which are given in ref 15b. The radius of energy capture by excimers was assumed to be equal to the mean distance between the chromophoric groups.[30] We have shown recently[31] that at room temperature the segmental reorientation time ($\tau_{rot} = k_{rot}^{-1}$) for PS $\tau_{rot} = 2.38 \times 10^{-10}$ s[8,32] is substantially longer than the time of energy hops between phenyl groups $\tau_{rot} \gg \tau_h$ ($\approx$1.4 ps). Recently Kyle and Kilp[33] obtained, on the basis of fluorescence quenching of PS in DCE by CCl_4, the time $\tau_h \approx 2.5$ ps. The inequality ($\tau_{rot} \gg \tau_h$) indicates that EM may be the decisive factor in the formation of intramolecular excimers in PS at room temperature. Thus, we have assumed k_{rot} for the investigated copolymers to be equal to 0. For other macromolecules, however, this statement may not be true.[4] The corresponding values of the coefficients of energy migration $\bar{\Lambda}$ were taken from our previous works,[15a,34] and their values are compiled in Table II.

The parameters used in the calculations were determined in independent experiments, apart from the concentration of EFS, q, whose value for every system was determined by way of best fit. The criterion to select the best fit was the minimization of the sum of squares of the differences between the theoretical and experimental values of Φ_M. The values of EFS are compiled in Table II and also presented in Figure 2 in the form of a plot as a function of the linkages between styrenes (f_{MM}) in a copolymer chain. The proportionality obtained between

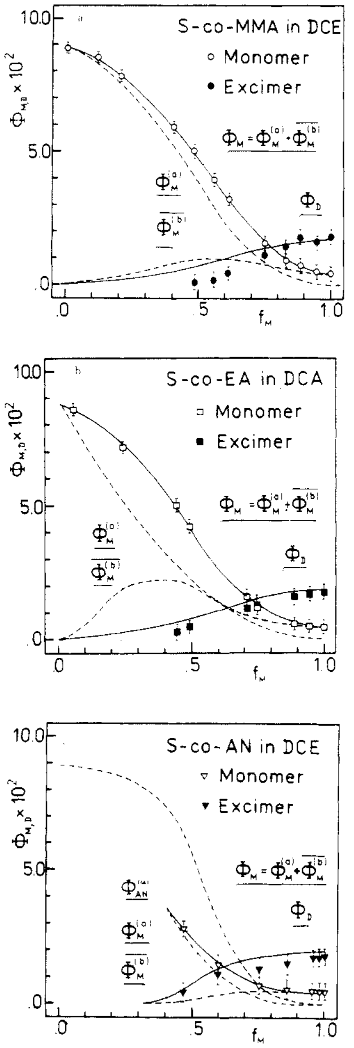

Figure 1. Experimental points and theoretical curves of quantum yields of monomer (Φ_M) and excimer (Φ_D) fluorescence of styrene copolymers in DCE at room temperature.

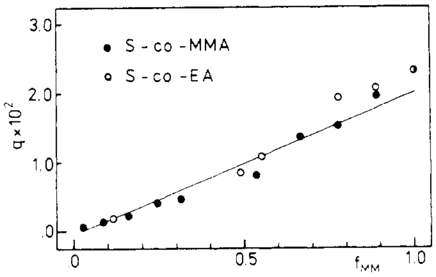

Figure 2. Excimer forming sites (q) in the function of the linkages between styrenes (f_{MM}) in a copolymer chain.

the fraction of excimer sites and the fraction of linkages between styrenes fully confirms the earlier hypothesis given by David et al.[16] and Reid and Soutar[17] and indicates that in copolymer S-*co*-MMA and S-*co*-EA intramolecular excimers are formed between neighboring chromophore groups.

The value of EFS ($q = 2.29 \times 10^{-2}$, see Table II) determined for PS is close to the values of EFS determined from fluorescence decays ($q = 1.73 \times 10^{-2}$)[9] and Monte Carlo simulations ($q = 2.8 \times 10^{-2}$).[35]

Table II
Photophysical Data for Styrene Copolymers in DCE

f_M	$A \times 10^8$, m^{2}s^{-1}	$\Phi_M \times 10^2$	$\Phi_D \times 10^2$	$q \times 10^2$
Styrene–Methyl Methacrylate				
1.000	1.03	0.45	1.80	2.290
0.945	1.15	0.50	1.60	1.960
0.885	1.25	0.70	1.75	1.510
0.830	1.40	0.90	1.40	1.380
0.758	1.65	1.50	1.10	0.818
0.620	1.78	3.20	0.45	0.471
0.565	1.95	3.90	0.20	0.411
0.485	2.56	5.00	0.10	0.243
0.405	3.82	5.90		0.144
0.209	3.75	7.80		0.159
0.126	3.50	8.50		0.076
0.011		8.90		
Styrene–Ethyl Acrylate				
1.000	1.03	0.45	1.80	2.29
0.943	1.09	0.50	1.70	2.07
0.888	1.19	0.60	1.60	1.85
0.749	1.45	1.20	1.35	1.11
0.709	1.56	1.60	1.20	0.76
0.495	1.83	2.80	0.50	0.83
0.445	2.31	4.10	0.30	0.22
0.241	3.01	5.40		
0.079		8.40		
Styrene–Acrylonitrile				
1.000	1.03	0.45	1.80	2.29
0.980	1.03	0.50	1.75	2.03
0.955	1.07	0.50	1.70	2.01
0.865	1.13	0.55	1.50	1.84
0.758	1.32	0.70	1.30	1.74
0.600	1.76	1.45	1.10	2.78
0.468	1.87	2.80	0.45	1.16

The changes of quantum yields of monomer fluorescence presented in Figure 1a,b may be divided into two domains. The observed drop of quantum yield of monomer fluorescence in the interval from about 0.5 to 1.0 of styrene mol fraction in copolymer may be interpreted as a result of intramolecular excimer formation, which leads to the quenching of monomer fluorescence. However, in the interval from about 0 to 0.5 of styrene mol fraction in the copolymer, the drop of Φ_M cannot be explained by the formation of excimers alone, whose concentration in this interval is very small. (See Table II.) It also cannot be explained by the changes of the EM coefficient.

Recently some authors[4,36] have suggested that in macromolecules the process of monomer fluorescence self-quenching takes place. Itagaki et al.,[37] in particular, in order to explain the differences in yields Φ_M obtained from the study of stationary and transient measurements of oligostyrene suggested the existence of intramolecular self-quenching by radiative migration.

In a number of papers[38,39] it was shown that the fluorescence self-quenching process as a result of absorption and secondary fluorescence may be neglected at the time when $cd\epsilon_{\max}$ is less than 0.1 (where c is the concentration of chromophoric groups, d is the optical path, and $\epsilon_{\max}$ is molar absorption coefficient. Due to the fact that in our investigations the product $cd\epsilon_{\max} \approx 0.08$, the process of self-quenching through reabsorption may be omitted.

The following processes may also be responsible for self-quenching:[40] (i) nonactive absorption of excitation light by dimers or molecules incapable of fluorescence; (ii) nonradiative energy transfer by way of migration or in a single step from excited monomers to nonexcited molecules as in point (i); (iii) energy transfer from excited to nonexcited monomers, though some of the transfers may lead to excitation energy scattering.

One must assume that the above-mentioned processes may take place simultaneously and their share in the process of fluorescence self-quenching depends on, among other things, the concentration of fluorescent molecules as well as the kind of solvent and the temperature.

Only the self-quenching of fluorescence by dimers has been thoroughly investigated experimentally (the inves-

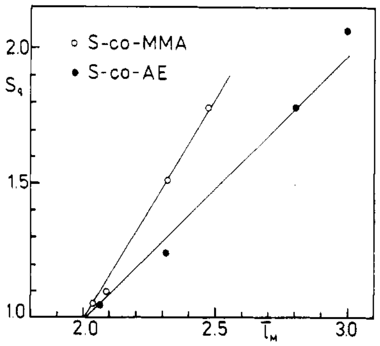

Figure 3. Self-quenching coefficient of monomer fluorescence as a function of mean styrene sequence ($\bar{l}_M$).

tigation of absorption bands, among others) and has a clear physical interpretation.[40,41] In the case of macromolecular systems, Irie et al.[42] found new absorption bands only for low molecular weight poly(1-vinylnaphthalene). In the case of oligostyrene, polystyrene and its copolymers, the UV absorption band, both with the poor and good solvents, was found to be substantially unchanged from that of alkylbenzene model compounds.[7b] This indicates that the formation of dimers in PS and its copolymers need not be taken into account.

Self-quenching by molecules supposedly incapable of fluorescence as well as quenching which takes place during energy transfer between monomers, process iii, are not fully understood.[43] It is presumed that the fluorescent molecule is incapable of fluorescence if there exists in the sphere of its influence a nonexcited molecule of the same kind.[44] Such so far vaguely defined interactions of fluorescent molecules may lead to a distortion of their potential surface in the excited state, as a result of which the energy is subject to internal conversion.[45]

The degradation of excitation energy during its transfer between monomers (monomer quenching) could, in particular, be the result of energy transfer to a molecule incapable of fluorescence. In this case, due to the small value of the radius of the sphere of influence,[44] process iii would lead to effective self-quenching of fluorescence only at high concentrations of chromophoric groups.

However, one already observes fluorescence self-quenching in the range of moderate chromophore group concentrations. (See Figure 1 and further discussion.)

It must be stressed that Makshantsev et al.[43] have recently shown that process iii may be significant also in the range of moderate concentration.

The presence of impurities may also affect excitation energy degradation. The recent investigations by Klöpffer[46] have shown that PS may contain a number of in-chain impurities, whose role in the processes of luminescence is not fully understood.

In the light of this short discussion, the physical interpretation of the process of fluorescence self-quenching in PS and its copolymers seems at present difficult. However, the existence of this process, as shown in our as well as other authors' investigations, seems proven, while a detailed analysis of this process requires further investigation.

Similar effects of self-quenching were observed recently for other synthetic macromolecules[4,36] and for chlorophylls as well.[47,48]

The phenomenological coefficient of self-quenching (S_q) may be defined by the equation

$$S_q = \Phi_M{}^{(b)*}/\bar{\Phi}_M{}^{(b)} \qquad (4)$$

where $\Phi_M{}^{(b)*}$ and $\bar{\Phi}_M{}^{(b)}$ are the fluorescence yields of monomers not subject to and subject to self-quenching, respectively. The values of S_q obtained from eq 4 are presented in Figure 3 as a function of mean styrene sequence length ($\bar{l}_M$) in copolymer. The proportionality of S_q to $\bar{l}_M$ so obtained indicates that the influence of methyl methacrylate or ethyl acrylate on the process of self-quenching of monomer fluorescence is secondary to quenching resulting from styrene–styrene interactions.

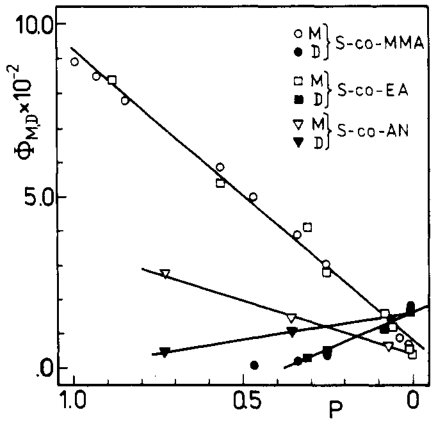

Figure 4. Quantum yields of monomer (Φ_M) and excimer (Φ_D) fluorescence as a function of the probability of finding an isolated styrene (P).

Copolymer of S-*co*-AN. Figure 1c shows the changes of monomer (Φ_M) and excimer (Φ_D) fluorescence yields of S-*co*-AN in DCE. Here also the theoretical changes of fluorescence yield of isolated styrene ($\Phi_{AN}{}^{(a)}$) in copolymer chain obtained under the assumption that the yield $\Phi_{AN}{}^{(a)} = 0.089$ for $P \rightarrow 0$ are presented by a broken line. As one may see, for $f_M \lesssim 0.75$ the calculated values of $\Phi_{AN}{}^{(a)}$ lie above the values of fluorescence yield obtained from the experimental study. This discrepancy may indicate that fluorescence yield of isolated styrene in S-*co*-AN is less than 0.089, the value obtained for S-*co*-MMA and S-*co*-EA. (See Figure 1a,b.)

Assuming that the isolated styrene chromophore emits only monomer fluorescence and that the nonisolated styrene can form excimers intramolecularly, the total monomer and excimer fluorescence yields are given by the formula

$$\Phi_M = P\Phi_M{}'^{(a)} + (1 - P)\bar{\Phi}_M{}'^{(b)} \qquad (5)$$

$$\Phi_D = (1 - P)\Phi_D{}' \qquad (6)$$

where $\bar{\Phi}_M{}'^{(b)}$ and $\Phi_D{}'$ are the quantum yields of monomer and excimer fluorescence for $P \rightarrow 0$ and $\Phi_M{}'^{(a)}$ is the quantum yield of monomer fluorescence for $P \rightarrow 1$. Figure 4 shows the changes of Φ_M and Φ_D, for the investigated copolymers, as a function of the probability of finding an isolated styrene in the copolymer chain. The linearity of this graph for S-*co*-MMA and S-*co*-EA indicates that both MMA and EA are totally nonpenetrative barriers for energy localized on an isolated styrene. This is understandable because of the small value of the critical radius for nonradiative energy migration between styrenes (R_{OMM}) compared with the minimal distance (R_{SS}) between isolated and nonisolated styrene in the copolymer chain ($R_{OMM} = 3.20$ Å[49] $< R_{SS} \approx 12$ Å). The investigations of energy transfer from the alternative S-*alt*-MMA to an acceptor in solution have led us to the same conclusion.[34]

Likewise, for S-*co*-AN the changes of Φ_M and Φ_D are also linear in the observed range of mole fraction of styrene in the copolymer (Figure 4). The value of $\Phi_M{}^{(a)}$ for S-*co*-AN in DCE cannot be determined experimentally due to the fact that DCE is a nonsolvent for acrylonitrile. The value of the yield of isolated styrene taken from Figure 4 for P

→ 1 equals 3.65×10^{-2}. Using this value we have to fit eq 1–3 to the experimental data of S-*co*-AN shown in Figure 1c. The calculations have been made for the same parameters (occurring in eq 1–3) as for S-*co*-MMA and S-*co*-AE, and the results are shown by broken and full lines in Figure 1c. The determined values of EFS were compiled in Table II. Although the quantum yield of isolated styrenes in S-*co*-AN was not determined experimentally, its value, determined in the way mentioned above, gave a satisfactory agreement with the presented theoretical model.

The comparison of EFS values, which are compiled in Table II for styrene copolymers, shows that these values are close, although in the case of S-*co*-AN, the monomer fluorescence yield is considerably lower compared with other compolymers. (See Figure 4.) We suppose that the intrachain interactions connected with a strong dipole moment for AN (4.29 D[50]) compared with the MMA (1.29 D[51]), EA (1.02 D[51]), and S (0.13 D[52]) dipole moments, is the main cause for the mentioned differences in the values of quantum yields. The interaction with DCE, which is a nonsolvent only for AN, may also lead to the drop of quantum yields of isolated styrenes.

Conclusions

The studies described in this paper have led to the following conclusions: (1) Energy migration occurs in polystyrene and its copolymers. (2) The concentration of excimer-forming sites (EFS) in styrene copolymers with methyl methacrylate and ethyl acrylate is proportional to the fraction of linkages between styrene species. (3) Apart from monomer fluorescence quenching by excimers, an additional process of monomer fluorescence self-quenching takes place in styrene copolymers.

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Appendix

In order to describe the excited-state kinetics of a macromolecule, we assume that excimers are formed as a result of two processes. The first is the energy migration with a rate constant in the form[31,34,53,54]

$$\bar{k}_{\mathrm{EM}}(t) = 4\pi\bar{\Lambda}r_{\mathrm{DD}}[(1 + r_{\mathrm{DD}})/(\pi\bar{\Lambda}t)^{1/2}] \qquad \text{(A1)}$$

where r_{DD} is the capture radius of excitation by excimers and $\bar{\Lambda}$ is the EM coefficient and the second is the segmental rotation about the backbone bond with a rate constant k_{rot}.

If one assumes that excimer dissociation is negligible, which is true for certain macromolecules,[4,37] the rates of concentrational changes of excited monomers ($N_{\mathrm{M}}^{(\mathrm{a})}(t)$, $\bar{N}_{\mathrm{M}}^{(\mathrm{b})}(t)$) and excimers ($N_{\mathrm{D}}(t)$) upon pulse excitation of a system at $t = 0$ can be described by the equations

$$\mathrm{d}N_{\mathrm{M}}^{(\mathrm{a})}(t)/\mathrm{d}t = -\tau_{\mathrm{OM}}^{-1}N_{\mathrm{M}}^{(\mathrm{a})}(t) \qquad \text{(A2)}$$

$$\mathrm{d}\bar{N}_{\mathrm{M}}^{(\mathrm{b})}(t)/\mathrm{d}t = -\tau_{\mathrm{OM}}^{-1}\bar{N}_{\mathrm{M}}^{(\mathrm{b})}(t) - \bar{k}_{\mathrm{EM}}(t)q\bar{N}_{\mathrm{M}}^{(\mathrm{b})}(t) - k_{\mathrm{rot}}q\bar{N}_{\mathrm{M}}^{(\mathrm{b})}(t) \qquad \text{(A3)}$$

$$\mathrm{d}N_{\mathrm{D}}(t)/\mathrm{d}t = -\tau_{\mathrm{OD}}^{-1}N_{\mathrm{D}}(t) + \bar{k}_{\mathrm{EM}}(t)q\bar{N}_{\mathrm{M}}^{(\mathrm{b})}(t) + k_{\mathrm{rot}}q\bar{N}_{\mathrm{M}}^{(\mathrm{b})}(t) \qquad \text{(A4)}$$

where q denotes concentration of excimer-forming sites (EFS) with the initial conditions

$$N_{\mathrm{M}}^{(\mathrm{a})}(0) = P \qquad \bar{N}_{\mathrm{M}}^{(\mathrm{b})}(0) = 1 - P \qquad N_{\mathrm{D}}(0) = 0 \qquad \text{(A5)}$$

Thus, total concentration of the excited monomers was assumed as $N_{\mathrm{M}}(0) = N_{\mathrm{M}}^{(\mathrm{a})}(0) + \sum_{i\geq 2}N_{\mathrm{M}_i}^{(\mathrm{b})}(0)P_i = 1$. P_i denotes the probability of finding a sequence with i monomeric units.

Due to the simplification that we have adopted in our model, mainly the substitution of the sequence of nonisolated monomers (diads, triads, etc.) by a mean value of a sequence l_{M}, the rate constant determined by eq A1 and the concentration of excited monomers (A3) are mean values (denoted by a bar over the terms) corresponding to the sequence $\bar{l}_{\mathrm{M}}$ for a copolymer of defined composition f_{M}.

Solving the system of eq A2–A4 with the initial conditions (A5) and the rate constant in the form of eq A1, we obtain

$$N_{\mathrm{M}}^{(\mathrm{a})}(t) = P\exp(-t/\tau_{\mathrm{OM}}) \qquad \text{(A6)}$$

$$\bar{N}_{\mathrm{M}}^{(\mathrm{b})}(t) = (1 - P)\exp(-t/\tau_{\mathrm{M}} - 2\Gamma_{\mathrm{M}}\tau_{\mathrm{M}}^{-1/2}t^{1/2}) \qquad \text{(A7)}$$

$$\begin{aligned} N_{\mathrm{D}}(t) = {} & (1 - P) \times \\ & (4\pi\bar{\Lambda}r_{\mathrm{DD}} + k_{\mathrm{rot}})q\Bigg\{\tau^{-1}[1 - \exp(-t/\tau_{\mathrm{M}} - 2\Gamma_{\mathrm{M}}\tau_{\mathrm{M}}^{-1/2}t^{1/2})] + \\ & \pi^{1/2}\tau^{-1/2}\exp(\Gamma_{\mathrm{M}}^2/(\tau_{\mathrm{M}}\tau)^2)\left(\frac{r_{\mathrm{DD}}}{(\pi\bar{\Lambda})^{1/2}} - \frac{\Gamma_{\mathrm{M}}}{(\tau_{\mathrm{M}}\tau)^{1/2}}\right)[\mathrm{erf}(\tau^{1/2}t^{1/2} + \Gamma_{\mathrm{M}}\tau_{\mathrm{M}}^{-1/2}\tau^{-1/2}) - \\ & \mathrm{erf}(\Gamma_{\mathrm{M}}\tau_{\mathrm{M}}^{-1/2}\tau^{-1/2})]\Bigg\}\exp(-t/\tau_{\mathrm{OD}}) \end{aligned} \qquad \text{(A8)}$$

where $\tau = \tau_{\mathrm{M}}^{-1} - \tau_{\mathrm{OD}}^{-1}$.

Defining the quantum yields of an isolated monomer ($\Phi_{\mathrm{M}}^{(\mathrm{a})}$), a nonisolated monomer ($\bar{\Phi}_{\mathrm{M}}^{(\mathrm{b})}$), and an excimer ($\Phi_{\mathrm{D}}$) by the relation

$$\begin{aligned} \Phi_{\mathrm{M}}^{(\mathrm{a})} &= k_{\mathrm{FM}}\int_0^\infty N_{\mathrm{M}}^{(\mathrm{a})}(t)\,\mathrm{d}t \\ \bar{\Phi}_{\mathrm{M}}^{(\mathrm{b})} &= k_{\mathrm{FM}}\int_0^\infty \bar{N}_{\mathrm{M}}^{(\mathrm{b})}(t)\,\mathrm{d}t \\ \Phi_{\mathrm{D}} &= k_{\mathrm{FD}}\int_0^\infty N_{\mathrm{D}}(t)\,\mathrm{d}t \end{aligned} \qquad \text{(A9)}$$

under the assumption that $\mathrm{erf}(\tau^{1/2}t^{1/2} + \Gamma_{\mathrm{M}}\tau_{\mathrm{M}}^{-1/2}\tau^{-1/2}) = 1$ for $t \to \infty$ we obtain, after substituting eq A6–A8 to the relation A9, eq 1–3.

Registry No. S-*co*-MMA, 25034-86-0; S-*co*-EA, 25066-97-1; S-*co*-AN, 9003-54-7.

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Upper Critical Solution Temperatures in Blends of Chlorinated Polyethylenes

Hiroyoshi Ueda and Frank E. Karasz*

Department of Polymer Science and Engineering, University of Massachusetts, Amherst, Massachusetts 01003. *Received May 6, 1985*

ABSTRACT: Upper critical solution temperatures, UCSTs, were found in binary blends of members of a series of high molecular weight chlorinated polyethylenes, CPE. Miscibilities were determined as a function of blend thermal history by measuring glass-transition temperatures by differential scanning calorimetry. As an example, derivative DSC curves for a 50/50 wt % blend of two CPEs containing respectively 42.2 and 50.7 wt % chlorine showed two peaks when the blend was annealed at 50 °C and one peak when the same blend was annealed at 130 °C. The reproducibility both of phase separation at lower temperatures and rehomogenization at higher temperatures was confirmed by cycling experiments. Phase diagrams of CPE blends showed maxima at 50/50 wt % compositions. The temperature of the UCST was found to depend primarily upon the difference in chlorine contents between the respective CPEs in the blends. In general the critical temperature was lowered as the chlorine content differences decreased, reflecting increased compatibility.

Introduction

Theoretical and experimental interest in miscibility of random copolymers with homopolymers or other copolymers has led to a number of predictions concerning the effects of structure, molecular weight, and temperature in these blends. One important class of mixtures is that in which the random copolymer $(A_xB_{1-x})_{n_1}$ is blended with a second copolymer containing the same monomeric moieties A and B but of different composition and molecular weight, e.g., $(A_yB_{1-y})_{n_2}$. In these formulas x and y represent mole fractions of A; n_1 and n_2 are the respective degrees of polymerization.

The zeroth-order mean-field prediction for this system is that miscibility (at any temperature) can occur only for the condition $|x - y| = 0$ if $n_1, n_2 = \infty$ and the segmental interaction χ_{AB} is greater than 0. If finite molecular weight polymers are employed, the maximum value for miscibility, $|x - y|_{\max}$, will itself be finite; moreover, the value of $|x -$

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