Macromolecules **1985,** *18,* 1015–1021

modes than the theoretical spectra expected from the Doi–Edwards theory.

Here, we should comment on the limitation of the blending law in its present form. The present law and presumably any other single function of a simple form cannot describe the behavior of binary blends covering whole ranges of the w_2 and M_{w2}/M_{w1} by the spectra of the components. As shown in our previous paper,[6] eq 10 for dilute blends and eq 11 for concentrated blends are valid only for the H, η_0, and $J_e{}^0$ of those with sufficiently large M_{w2}/M_{w1} ratios (presumably ≥ 8), while eq 12 seems to hold only for those with M_{w2}/M_{w1} ratios very close to unity (presumably <1.8, which is the value for the L294/L161 blend).

At present, we do not have a blending law of a definite form covering these two extremes of eq 10 and 11 and eq 12. This is due to the fact that entanglements for a chain in a blend may depend on w_2, M_{w2}, and M_{w2}/M_{w1} ratio, and differ from those in its bulk. To obtain a blending law covering whole ranges of these quantities, we must at first determine the relaxation spectrum of a chain placed in such a particular entanglement state.[24] Recently, such an attempt has been made but is unfortunately not yet successful.[25]

If we rely on the tube model, we must consider complicated processes, in which the reptation of a chain with fluctuating contour length, the tube renewal process, and other possible molecular motions take place cooperatively in a complicated fashion. A study on ternary blends and polydisperse polymers having a broad and continuous MWD has been undertaken. Such a study will clarify this problem to some extent, although an analysis of such complicated processes would be very difficult.

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Synthesis and Viscosity Studies of Some Novel Ionene Polymers

Edward G. Knapick, Jerry A. Hirsch,* and Paul Ander*

Department of Chemistry, Seton Hall University, South Orange, New Jersey 07079.
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ABSTRACT: To probe polyelectrolyte–polysoap transitions, three series of N,N-disubstituted ionenes have been prepared differing in their charge separation by having three, four, or six methylenes between the charged quaternary nitrogens. In each series, one N-substituent is methyl, while the other is methyl, ethyl, *n*-butyl, *n*-hexyl, or *n*-octyl. Ultrafiltration studies were performed to establish that all polymers range in molecular weight between 10 000 and 40 000. Viscosities were obtained in salt and salt-free solutions of water and ethanol–water mixtures. For smaller alkyl groups, the shapes of the curves were typical for polyelectrolytes. As the length of the *N*-alkyl increases, both the overall reduced viscosities and the steepness of the curves decreased, indicating polysoap behavior. The order of viscosities in several aqueous ethanol mixtures showed analogous changes. The charge density of the polyelectrolyte seems less important than the length of the pendant alkyl group in the onset of this transition.

Introduction

Polysoaps[1] are an interesting and useful subclass of polyelectrolytes. In general, a polysoap can be defined as a polymer in which soap molecules are part of the covalent structure.

In the course of work on counterion diffusion utilizing a series of ionene structures,[2] it became of interest to develop a new class of ionenes called ionene polysoaps[3] (**1**). These ionenes, polyelectrolytes in which the charges in the backbone are well-defined, would incorporate aliphatic,

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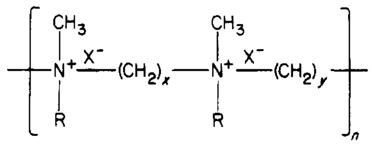


1

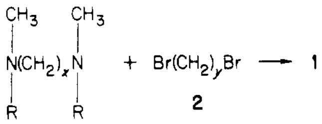
R	x = y			
	3	4	5	6
methyl	1a	1f		1k
ethyl	1b	1g		1l
n-butyl	1c	1h		1m
n-hexyl	1d	1i		1n
n-octyl	1e	1j		1o
n-dodecyl	1p		1q	
n-octadecyl			1r	

nonpolar branches in the repeating unit of the polyelectrolytes being studied. Sonnessa et al.[3] synthesized **1p**, **1q**, and **1r**. For simplicity, these are named 33R12, 55R12, and 55R18, respectively. Viscosity results indicated (1) that these compounds are more compact the higher the polarity of the solvent, (2) that this compactness is more dependent on the length of the alkyl chain than on charge density, and (3) in the more apolar solvents, that this compactness is independent of the length of the alkyl group as long as $R \geq 12$.

The current work involves an extension of these findings in order to more clearly define the transition from polyelectrolyte to polysoap.[4] Toward this end ionenes **1a–o** were synthesized and their viscosity behavior was studied. In this way the effect of both the length of the alkyl group and the charge separation could be studied. It is expected that those which are polyelectrolytes will have higher viscosities in the higher dielectric media, while the viscosities of the polysoaps in the same media will decrease.

Results and Discussion

Synthesis. Synthesis of all ionenes was accomplished via Menshutkin reactions (eq 1). The synthesis of the necessary diamines has been previously reported.[5]



$$\mathrm{CH_3(R)N(CH_2)_xN(R)CH_3} + \mathrm{Br(CH_2)_yBr} \longrightarrow \mathbf{1} \qquad (1)$$

Conditions for the polymerization of ionenes with short alkyl groups were reported by Rembaum[6] as follows: DMF/MeOH (1:1 or 4:1) as solvent; total concentration of 3.0 M (1.5 M in each monomer); and a 5–7-day reaction time. It was recognized that as the length of the N-substituted alkyl group increased, the transition state, as well as the product, would have more apolar character. Therefore, time, temperature, concentration, and solvent were varied for each of the ionene systems investigated in order to find the "best" conditions for each (as measured by product viscosity). It was found that, except for solvent, the original conditions worked well for all ionenes synthesized. As might be expected, those ionenes with shorter alkyl groups polymerize best in higher dielectric media, while those with longer alkyl groups polymerize as well in solvents of low polarity. Specifically, all the R8 compounds (i.e., those where R = *n*-octyl) and 33R6 (**1d**) fell into this latter category.

Ultrafiltration. After optimizing the conditions for each individual ionene, it was next necessary to judge whether all the ionenes could be said to be in the same molecular weight range. Ultrafiltration was chosen as a convenient method of fractionation and characterization.[7] Here, a 0.05% solution of each polymer was passed through an Amicon Model 202 stirred cell fitted with a nominal 10 000 molecular weight cutoff membrane. Viscosities of the retained polymer were then compared to those determined before filtration. Results are shown in Table I. It is assumed that if the viscosity does not change, and if a consistently large amount of polymer is retained, then the original product is at least approximately 10 000 molecular weight. This presumes (a) that the ionenes do not clog or bind to the membrane and (b) that the size grading done by the membrane reflects molecular weight differences.

Table I

polymer	membrane	initial $[\eta]^a$	% retained	retained $[\eta]^a$
66R1	PM 10	0.268	90	0.293
66R2	PM 10	0.142	81	0.136
66R4	PM 10	0.105	83	0.119
66R6	YM 10	0.209^b	62	0.324^b
66R8	YM 10	0.075^c	50	0.098^c
44R2	PM 10	0.095	83	0.096
44R2	YM 10	0.095	76	0.112
44R4	PM 10	0.084	87	0.090
44R4	YM 10	0.084	59	0.095
44R6	YM 10	0.130^d	60	0.336^d
44R8	YM 10	0.068^c	36	0.117^e
34R1	YM 10	0.196	90	0.219
33R4	YM 10	0.056	39	0.063
33R6	YM 10	0.048^b	33	0.055^b
33R8	YM 10	0.051^f	63	0.060^f
66R1	PM 30	0.268	76	0.258
34R1	YM 30	0.196	86	0.197

[a] Intrinsic viscosity in 0.4 M KBr. [b] Insoluble in 0.4 M KBr; η_{red} compared at 1.0 g/dL (50% EtOH, 5×10^{-3} M KBr). [c] Insoluble in 0.4 M KBr; η_{red} compared at 1.0 g/dL (50% EtOH, 5×10^{-3} M KBr). [d] Insoluble in 0.4 M KBr; η_{red} compared at 1.0 g/dL H_2O. [e] Insoluble in 0.4 M KBr; η_{red} compared at 0.5 g/dL (70% EtOH, 5×10^{-3} M KBr). [f] Insoluble in 0.4 M KBr; η_{red} compared at 1.0 g/dL (70% EtOH, 5×10^{-3} M KBr).

To check for clogging, the filtrate was passed back through the same membrane. The percentage of material retained from this was then compared to that found in the original retainate. If the percentage in the former is greater than that of the latter, then the membrane is clogged. Clogging was observed when PM10 (nominal 10 000 molecular weight cutoff) membranes were used for 66R6 and 66R8 (**1n** and **1o**). When YM10 membranes were used, this did not happen. All other ionenes showed no evidence of clogging. Therefore, all R6 and R8 ionenes were filtered with YM type membranes. For the other ionenes, the YM and PM series gave similar retainate viscosity and percent retainate (see 44R2 in Table I).

The nominal molecular weight cutoffs of the membrane are actually based on size rather than molecular weight. Therefore, two ionenes (34R1 and 66R1) for which the Mark–Houwink parameters K and a are known[8] (eq 2 and 3, respectively) were passed through ultrafilters. From the

$$[\eta] = 2.94 \times 10^{-4} M^{0.61} \qquad \text{(for 34R1)} \qquad (2)$$

$$[\eta] = 6.22 \times 10^{-4} M^{0.58} \qquad \text{(for 66R1)} \qquad (3)$$

equations for the 3,4 and 6,6 respectively, the M_v values were found to be 42 000 (34R1) and 35 000 (66R1). The 34R1 ionene was synthesized according to the procedure of Rembaum. Both of these ionenes were found to be retained by both 10 000 and 30 000 molecular weight membranes with no appreciable change in viscosity.

As a final check on the method, two separate trials of the same polymer (44R6) were compared before and after ultrafiltration. The original viscosities in H_2O at 0.50 g/dL were 0.164 (trial 1) and 0.360 (trial 2) dL/g. After each was passed through a YM10 membrane, the resulting viscosities were 0.392 (trial 1) and 0.460 (trial 2) dL/g.

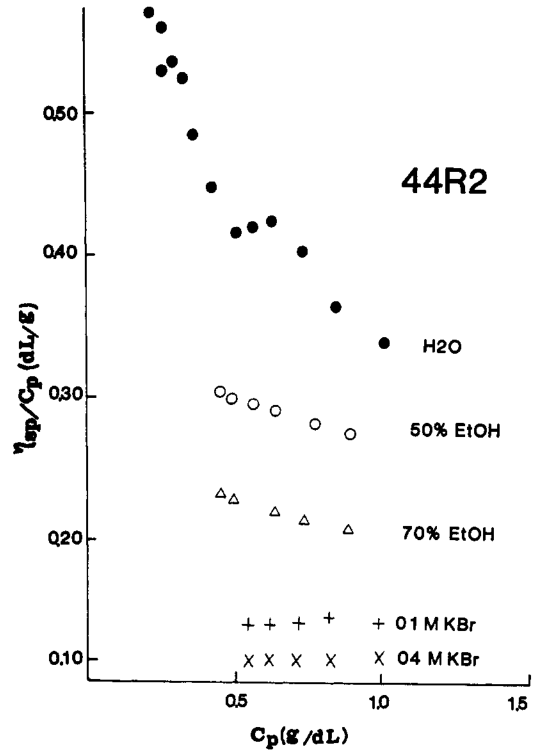


Figure 1. Concentration dependence on the reduced viscosity for 44R2 in several solvents.

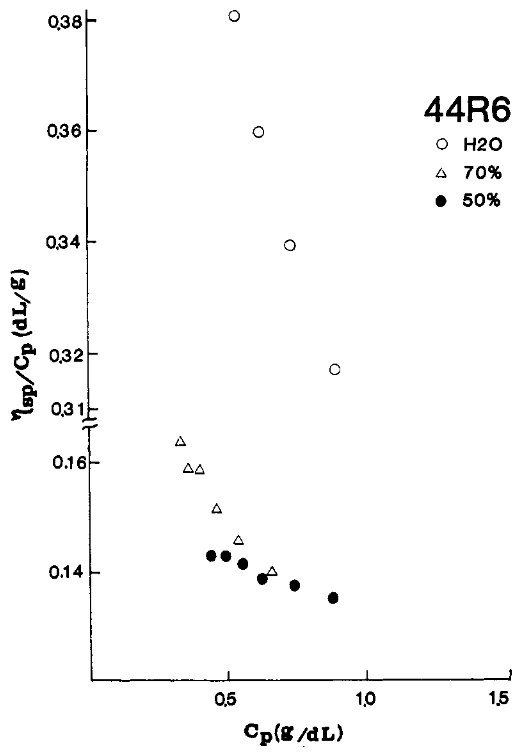


Figure 3. Concentration dependence on the reduced viscosity for 44R6 in water and 50% and 70% ethanol.

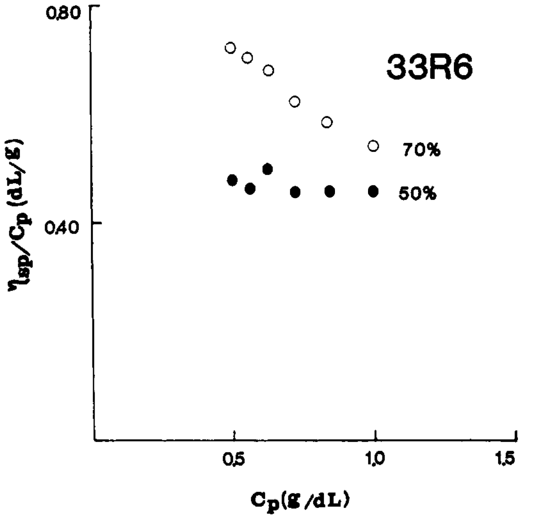


Figure 2. Concentration dependence on the reduced viscosity for 33R6 in 50% and 70% ethanol.

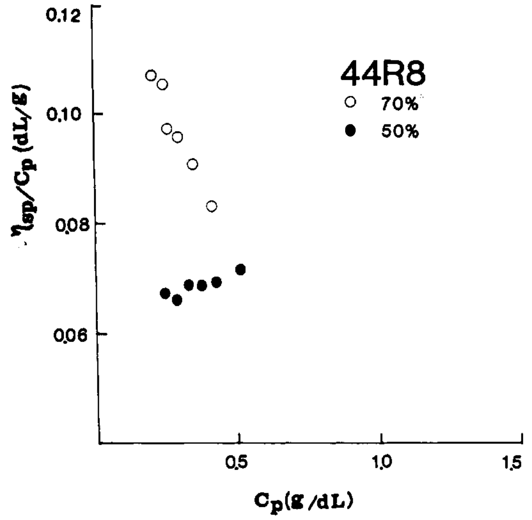


Figure 4. Concentration dependence on the reduced viscosity for 44R8 in 50% and 70% ethanol.

Since the resulting viscosities were much closer than the original values, the membrane was not merely cutting off an arbitrary percentage of the sample, but was making a size discrimination. All ionenes tested passed through a 10 000 molecular weight membrane with no significant change in viscosity except 44R6, 44R8, and 66R8 (see Table I). For these, only the retainate was used for the viscosity studies.

The important conclusions reached from these data are that the compounds are at least approximately 10 000 molecular weight and that the viscosity results discussed below are not based on vastly different degrees of polymerization.

Viscosity. Viscosities of the various ionenes were determined in H_2O, 50% aqueous EtOH, 70% aqueous EtOH, and 0.1 and 0.4 N aqueous KBr solutions. It was found that normal polyelectrolyte behavior was observed for all ionenes with R groups from methyl to *n*-butyl in the 33 and 44 series and from methyl to *n*-hexyl in the 66 series.

Normal polyelectrolyte behavior means that typified by the curves for the 44R2 ionene in Figure 1. As the concentration of the polymer decreases in salt-free or extremely dilute salt solutions, the charges on the backbone become less shielded by the counterions, leading to an increase in intramolecular repulsion. This caused the polymer to expand, resulting in a dramatic rise in reduced viscosity as shown in Figure 1. As the percentage of EtOH in the viscosity solvent is increased, the solvent polarity decreases and so, therefore, do the ionic interactions of the macroion. The result is the viscosity of the 44R2 decreases in the order H_2O > 50% EtOH > 70% EtOH. In strong electrolyte solutions such as 0.1 and 0.4 N KBr, 44R2 behaves as a nonionic solute.

In the 33 series we begin to see some behavior not typical of a polyelectrolyte when R = *n*-hexyl (Figure 2). Here

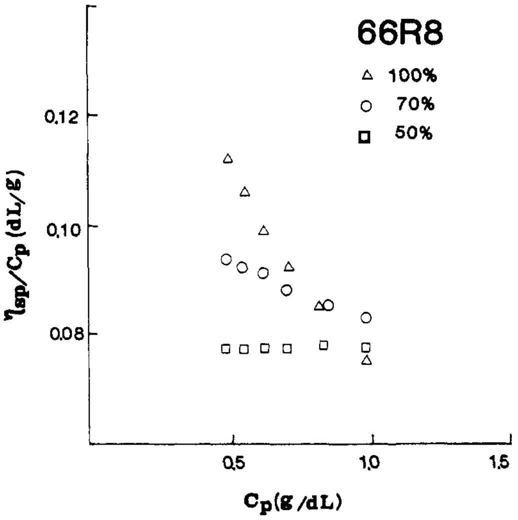


Figure 5. Concentration dependence on the reduced viscosity for 66R8 in 50%, 70%, and 100% ethanol.

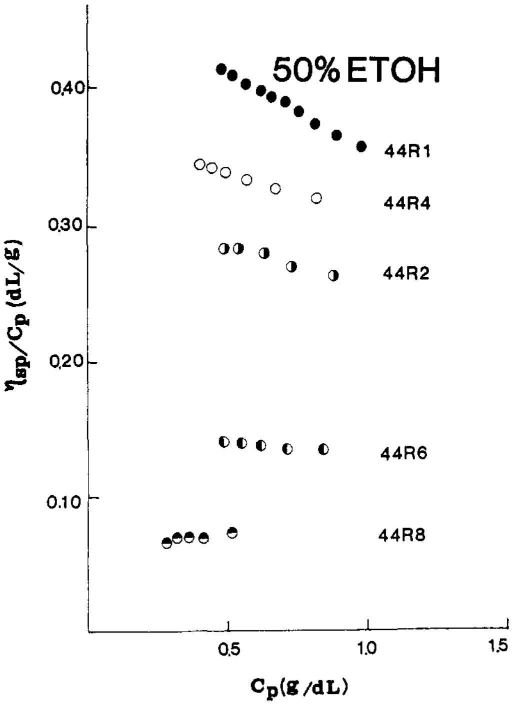


Figure 6. Concentration dependence on the reduced viscosity for 44R1, 44R2, 44R6, and 44R8 in 50% ethanol.

the η_{red} values are higher in the less polar 70% EtOH than in 50% EtOH.

In the 44 series, the R6 shows typical polyelectrolyte behavior in H_2O, but the η_{red} is slightly higher in the 70% EtOH than in 50% EtOH (Figure 3). The R8 shows the same atypical behavior in EtOH solutions (Figure 4).

For the 66R8 ionene (Figure 5) the η_{red}'s increase in the order 50% EtOH < 70% EtOH < absolute EtOH.

While no apparent break is seen in the 33 series, looking at the viscosities of the 44 ionenes in 50% EtOH (Figure 6), there is a large drop in reduced viscosity when going from R4 to R6. The same can be seen in the 66 series (Figure 7), with a large drop in going to the R8 ionene.

Conclusions

At some point in each of these series, as the alkyl group is lengthened, polysoap behavior becomes apparent, with a corresponding large drop in viscosity. In the 44 series, this happens with *N*-*n*-hexyl substitution. In the 66 series, this occurs with *N*-*n*-octyl substitution.

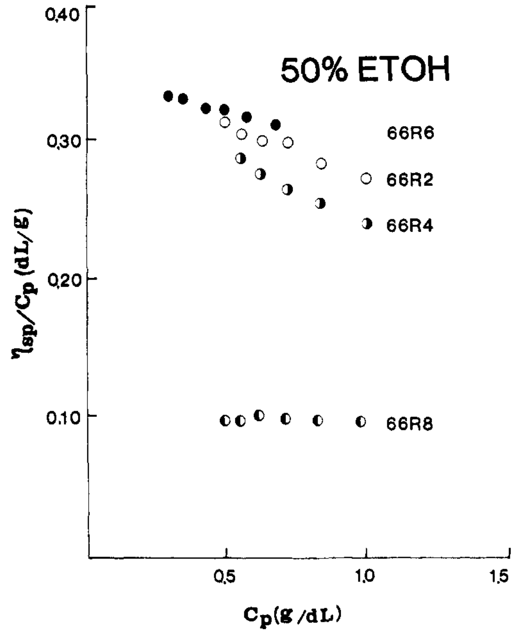


Figure 7. Concentration dependence on the reduced viscosity for 66R2, 66R4, 66R6, and 66R8 in 50% ethanol.

These "break points" correspond to those ionenes that show a change in the order of viscosities in the EtOH solvents. This is probably due to hydrophobic interactions becoming dominant at this point, causing the polymer to be more compact as the polarity of the solvent increases. Therefore, we can say that in the ionene system, the transition from polyelectrolyte to polysoap occurs when R = *n*-hexyl for the 33 and 44 series, and when R = *n*-octyl in the 66 series.

It is interesting that, as in the Sonnessa[3] work, the charge density seems to be less important than the length of the alkyl group. That is, in the higher charge density 33 and 44 series, polysoap behavior (as evidenced by viscosity decrease) is seen with shorter alkyl groups (R6) than in the lower charge density 66 series (R8).

Experimental Section

All melting points were determined in open capillary tubes by using a Mel-Temp apparatus and are uncorrected. All boiling points are uncorrected. The elemental analyses were performed by Analytische Laboratorien, Elback, Germany. The infrared spectra were taken on a Perkin-Elmer Model 567 grating infrared spectrophotometer. Liquids were run as thin films; solids were recorded as Nujol mulls unless otherwise stated. The nuclear magnetic resonance spectra were determined on a Varian Model T-60 recording spectrometer at 60 MHz at room temperature. The solvent for all nonpolymeric materials was deuteriochloroform ($CDCl_3$) and that for all polymers was deuterium oxide unless otherwise indicated. Tetramethylsilane Me_4Si was used as the internal standard in $CDCl_3$ and methanol-d_4 and 3-(trimethylsilyl)propanesulfonic acid (DSS) was used as the internal standard in D_2O and Me_2SO-d_6. All signals are given in parts per million (δ) relative to Me_4Si or DSS.

All viscosity measurements were carried out in an Ubbelhode viscometer at 25.0 ± 0.1 °C. The bulb was filled with 10 mL of solution and then diluted in 2-mL increments to a total volume of 20 mL.

General Procedure for Polymerization. Exactly equal molar amounts of the freshly distilled diamine and dihalide were thoroughly mixed with sufficient solvent to make the total concentration 3.0 M. The solution was then poured into a round-bottom flask and stirred at room temperature for several days or until the whole mixture became solid. Those which did not solidify became very thick gumlike liquids. These were dissolved in MeOH, poured into a larger round-bottom flask, placed on a rotary evaporator, and then vacuum pumped until they solidified.

Each polymer was precipitated several times by dissolving the solid in a minimum amount of either $\mathrm{H_2O}$ or MeOH (depending on solubility). This solution was then passed through a gravity filter, the filtrate dripping into a large amount of nonsolvent (acetone or toluene). The liquid was decanted and the solid polymer dried in a vacuum oven at 50 °C.

Poly[(dimethylimino)propylene bromide], 33R1 (1a). A mixture of 1.3024 g (10 mmol) of *N,N,N′,N′*-tetramethyl-1,3-propanediamine (Aldrich) and 2.0190 g (10 mmol) of 1,3-dibromopropane was treated in the above manner for 8 days with enough DMF/MeOH (1:1) as solvent to give a final volume of 7.0 mL. Water/acetone was used as the precipitation medium to yield 1.53 g (46%) of a white solid: NMR δ 2.5 (broad m, 2 H, $\mathrm{N^+CCH_2CN^+}$), 3.3 (s, 6 H, $\mathrm{N^+CH_3}$), 3.6 (broad m, 4 H, $\mathrm{N^+CH_2CCH_2N^+}$).

Poly[(methylethylimino)propylene bromide], 33R2 (1b). Enough MeOH was added to 1.5828 g (10 mmol) of the required diamine[5] and 2.0190 g (10 mmol) of 1,3-dibromopropane to give a total volume of 6.8 mL. This was treated in the above manner for 5 days with $\mathrm{H_2O}$/acetone as the precipitating media, to give 3.23 g (90%) of a white solid: NMR δ 1.4 (broad t, 3 H, $\mathrm{CH_3C}$), 2.5 (broad m, 2 H, $\mathrm{N^+CCH_2CN^+}$), 3.2 (s, 3 H, $\mathrm{N^+CH_3}$), 3.6 (broad m, 6 H, $\mathrm{CH_2N^+CH_2CCH_2CN^+}$).

Poly[(methylbutylimino)propylene bromide], 33R4 (1c). To a mixture of 2.1439 g (10 mmol) of the required diamine[5] and 2.0190 g (10 mmol) of 1,3-dibromopropane was added enough DMF/MeOH (4:1) to give a total volume of 6.7 mL. This was treated in the above manner for 8 days. After precipitation with $\mathrm{H_2O}$/acetone, 1.8 g (42%) of a white powder was obtained: NMR δ 1.1 (broad t, 3 H, $\mathrm{CH_3C}$), 1.6 (broad m, 4 H, $\mathrm{CH_3(C\mathit{H}_2)_2}$), 2.5 (broad m, 2 H, $\mathrm{N^+CCH_2CN^+}$), 3.4 (s, 3 H, $\mathrm{N^+CH_3}$), 3.7 (broad m, 6 H, $\mathrm{Ch_2N^+CH_2CCH_2N^+}$).

Anal. Calcd for $\mathrm{C_{18}H_{18}NBr}$: C, 46.16; H, 8.72; N, 6.73; Br, 38.39. Found: C, 45.03; H, 8.67; N, 6.54; Br, 37.63. N/Br = 1.0. Analysis is correct if we assume $\mathrm{C_8H_{18}NBr\cdot{}^1/_4H_2O}$.

Poly[(methylhexylimino)propylene bromide], 33R6 (1d). A solution of 2.7050 g (10 mmol) of the diamine[5] and 2.0190 g (10 mmol) of 1,3-dibromopropane in sufficient MeOH to give a total volume of 6.7 mL was treated in the above manner for 9 days. With acetone as an additional wash of the solid, 4.0 g (85%) of a white solid was obtained: NMR (methanol-d_4) δ 1.0 (broad t, 3 H, $\mathrm{CH_3C}$), 1.2–2.0 (overlapping m, 8 H, $\mathrm{CH_3(C\mathit{H}_2)_4}$), 2.6 (broad m, 2 H, $\mathrm{N^+CCH_2CN^+}$), 3.4 (s, 3 H, $\mathrm{N^+CH_3}$), 3.7 (broad m, 6 H, $\mathrm{CH_2N^+CH_2CCH_2N^+}$).

Poly[(methyloctylimino)propylene bromide], 33R8 (1e). To a mixture of 3.2661 g (10 mmol) of the requisite diamine[5] and 2.0190 g (10 mmol) of 1,3-dibromopropane was added enough MeOH/hexane (5:2) to give a total volume of 6.7 mL. This was stirred for 5 days. After the solid was washed with acetone and dried, 4.6 g (86%) of a yellow solid was obtained: NMR (methanol-d_4) δ 1.0 (t, 3 H, $\mathrm{CH_3C}$), 1.4 (broad m, 12 H, $\mathrm{CH_3(C\mathit{H}_2)_6}$), 2.6 (broad m, 2 H, $\mathrm{N^+CCH_2CN^+}$), 3.4 (s, 3 H, $\mathrm{N^+CH_3}$), 3.7 (broad m, 6 H, $\mathrm{CH_2N^+CH_2CCH_2N^+}$).

Poly[(dimethylimino)butylene bromide], 44R1 (1f). A mixture of 1.4426 g (10 mmol) of the required diamine (Aldrich) and 2.1593 g (10 mmol) of 1,4-dibromobutane in sufficient DMF/MeOH (1:1) to give a total volume of 7 mL was treated as above. Within 3 h, all the material in the reaction flask was solid. With $\mathrm{H_2O}$/acetone as the reprecipitating agent, 1.9 g (52%) of a white solid was obtained: NMR δ 1.9 (broad m, 4 H, $\mathrm{N^+C(C\mathit{H}_2)_2CN^+}$), 3.2 (s, 6 H, $\mathrm{N^+CH_3}$), 3.5 (m, 4 H, $\mathrm{N^+CH_2(C)_2CH_2N^+}$).

Poly[(methylethylimino)butylene bromide], 44R2 (1g). A mixture of 1.7231 g (10 mmol) of the requisite diamine[5] and 2.1593 g (10 mmol) of 1,4-dibromobutane in sufficient DMF/MeOH (1:1) to give a total volume of 7 mL was treated in the above manner for 7 days. With $\mathrm{H_2O}$/acetone as the reprecipitating agent, 2.8 g (72%) of a light tan solid was obtained: NMR δ 1.3 (broad m, 3 H, $\mathrm{CH_3C}$), 1.9 (broad m, 4 H, $\mathrm{N^+C(CH_2)_2CN^+}$), 3.0 (s, 3 H, $\mathrm{N^+CH_3}$), 3.4 (broad m, 6 H, $\mathrm{CH_2N^+CH_2(C)_2CH_2N^+}$).

Poly[(methylbutylimino)butylene bromide], 44R4 (1h). A mixture of 2.2842 g (10 mmol) of the required diamine[5] and 2.1593 g (10 mmol) of 1,4-dibromobutane in enough DMF/MeOH (1:1) for a total volume of 6.7 mL was treated as above for 8 days. With $\mathrm{H_2O}$/acetone as the precipitation media (with additional pentane washes), 3.5 g (78%) of a light yellow-tan solid was obtained: NMR δ 1.0 (distorted t, 3 H, $\mathrm{H_3CC}$), 1.9 (broad m, 8 H, $\mathrm{CH_3(C\mathit{H}_2)_2CN^+}$), 3.2 (s, 3 H, $\mathrm{N^+CH_3}$), 3.5 (broad m, 6 H, $\mathrm{CH_2N^+CH_2(C)_2CH_2N^+}$).

Anal. Calcd for $\mathrm{C_9H_{20}NBr}$: C, 48.88; H, 9.02; N, 6.30; Br, 35.97. Found: C, 46.76; H, 8.75; N, 6.18; Br, 34.81. N/Br = 1.0. Analysis is correct if we assume $\mathrm{C_9H_{20}NBr\cdot{}^1/_2H_2O}$.

Poly[(methylhexylimino)butylene bromide], 44R6 (1i). Trial 1. A mixture of 2.8453 g (10 mol) of the methylhexyl diamine[5] and 2.1593 g of 1,4-dibromobutane (10 mmol) was dissolved in sufficient benzene to give a total volume of 14 mL. After this was stirred and warmed for 11 days, 4.3 g of a yellowish-tan solid was obtained: NMR (methanol-d_4) δ 1.0 (distorted t, 3 H, $\mathrm{CH_3C}$), 1.4 (broad m, 8 H, $\mathrm{CH_3(C\mathit{H}_2)_4}$), 1.8 (broad m, 4 H, $\mathrm{N^+C(CH_2)_2CN^+}$), 3.1 (s, 3 H, $\mathrm{N^+CH_3}$), 3.4 (broad m, 6 H, $\mathrm{CH_2N^+CH_2(C)_2CH_2N^+}$).

Trial 2. MeOH was used as the solvent and the solution was stirred for 14 days. After an additional wash with pentane, 2.38 g (47%) of a sticky yellow solid was obtained.

Poly[(methyloctylimino)butylene bromide], 44R8 (1j). A mixture of 3.4063 g (10 mmol) of the required diamine[5] and 2.1593 g (10 mmol) of 1,4-dibromobutane was dissolved in sufficient anhydrous MeOH to give a total volume of 13.3 mL. After the solution was stirred for 9 days, 4.48 g (80%) of a light yellow solid was obtained after reprecipitation with MeOH/toluene and an additional wash with pentane: NMR ($\mathrm{CDCl_3}$) δ 0.9 (distorted t, 3 H, $\mathrm{CH_3C}$), 1.3 (broad m, 12 H, $\mathrm{CH_3(C\mathit{H}_2)_6}$), 2.0 (broad m, 4 H $\mathrm{N^+C(CH_2)_2CN^+}$), 3.2 (s, 3 H, $\mathrm{N^+CH_3}$), 3.7 (m, 6 H, $\mathrm{CH_2N^+CH_2(C)_2CH_2N^+}$).

Poly[(dimethylimino)hexylene bromide], 66R1 (1k). A mixture of 6.883 g (40 mmol) of *N,N,N′,N′*-tetramethyl-1,6-hexanediamine (Aldrich) and 9.7584 g (40 mmol) of 1,6-dibromohexane (Aldrich) was dissolved in sufficient DMF/MeOH (1:1) to give a total volume of 27 mL. After 2 days, the white solid was reprecipitated with $\mathrm{H_2O}$/acetone to give 8.7 g (71%) of a dry white powder: NMR δ 1.67 (m, 8 H, $\mathrm{N^+C(CH_2)_4CN^+}$), 3.03 (s, 6 H, $\mathrm{N^+CH_3}$), 3.2 (m, 4 H, $\mathrm{N^+CH_2(C)_4CH_2N^+}$).

Poly[(methylethylimino)hexylene bromide], 66R2 (1l). A mixture of 6.0104 g (30 mmol) of the required diamine[5] and 7.3194 (30 mmol) of 1,6-dibromohexane was dissolved in enough DMF/MeOH (3:1) for a final volume of 7 mL and stirred for 5 days. After reprecipitation from $\mathrm{H_2O}$/acetone, 2.99 g (66%) of a white solid was isolated: NMR δ 1.4 (broad m, 11 H, $\mathrm{N^+C(CH_2)_4CN^+ + CH_3C}$), 3.0 (s, 3 H, $\mathrm{N^+CH_3}$), 3.3 (m, 6 H, $\mathrm{CH_2N^+CH_2(C)_4CH_2N^+}$).

Poly[(methylbutylimino)hexylene bromide], 66R4 (1m). A mixture of 2.5648 g (10 mmol) of the required methylbutyl diamine[5] and 2.4398 g (10 mmol) of 1,6-dibromohexane was dissolved in sufficient anhydrous MeOH for a final volume of 10 mL and stirred for 7 days. After reprecipitation from $\mathrm{H_2O}$/acetone, and stirring with pentane, 3.5 g (71%) of a white solid was obtained: NMR δ 1.0 (distorted t, 3 H, $\mathrm{CH_3C}$), 1.6 (broad m, 12 H, $\mathrm{CH_3(C\mathit{H}_2CN^+C(C\mathit{H}_2)_4}$), 3.0 (s, $\mathrm{N^+CH_3}$), 3.3 (m, 6 H, $\mathrm{CH_2N^+CH_2(C)_4CH_2N^+}$).

Anal. Calcd for $\mathrm{C_{11}H_{24}NBr}$: C, 52.80; H, 9.67; N, 5.60; Br, 31.93. Found: C, 49.10; H, 9.64; N, 5.06; Br, 30.28 N/Br = 0.95. Analysis is correct if we assume $\mathrm{C_{11}H_{24}NBr\cdot H_2O}$.

Poly[(methylhexylimino)hexylene bromide], 66R6 (1n). A mixture of 3.1258 g (10 mmol) of the required diamine[5] and 2.4398 g (10 mmol) of 1,6-dibromohexane is dissolved in enough anhydrous MeOH for a final volume of 6.7 mL and stirred for 9 days. After reprecipitation with MeOH/toluene, 3.73 g (67%) of a white solid was obtained: NMR (methanol-d_4) δ 1.0 (distorted t, 3 H, $\mathrm{CH_3C}$), 1.6 (distorted m, 16 H, $\mathrm{CH_3(C\mathit{H}_2)_4CHN^+C(C\mathit{H}_2)_4}$), 3.2 (s, 3 H, $\mathrm{N^+CH_3}$), 3.6 (broad m, 6 H, $\mathrm{CH_2N^+CH_2(C)_4CH_2N^+}$).

Poly[(methyloctylimino)hexylene bromide], 66R8 (1o). A mixture of 7.3738 g (20 mmol) of the required diamine[5] and 4.8796 g (20 mmol) of 1,6-dibromohexane was dissolved in sufficient $\mathrm{CH_2Cl_2}$ to make a total of 13.3 mL of solution. After the solution was stirred for 10 days, the product was reprecipitated with MeOH/toluene and stirred with pentane. This resulted in 3.16 g (26%) of a white solid: NMR ($\mathrm{Me_2SO}$-d_6) δ 1.0 (distorted t, 3 H, $\mathrm{CH_3C}$), 1.5 (broad m, 20 H, $\mathrm{CH_3(C\mathit{H})_6CN^+C(C\mathit{H}_2)_4}$), 3.2 (s, 3 H, $\mathrm{N^+CH_3}$), 3.6 (m, 6 H, $\mathrm{CH_2N^+CH_2(C)_4CH_2N^+}$).

Poly[(dimethylimino)propylene(dimethylimino)butylene bromide], 34R1. A mixture of 2.6048 g (20 mmol) of *N,N,N′,-N′*-tetramethyl-1,3-propanediamine and 4.3186 g (20 mmol) of

1,4-dibromobutane in sufficient DMF/MeOH (1:1) to give a final volume of 13.3 mL was stirred for 5 days yielding 5.7 g (82%) of a white solid after reprecipitation from H_2O/acetone: NMR δ 2.0 (broad m, 4 H, $N^+C(CH_2)_2CN^+$), 2.5 (broad m, 2 H, N^+-CCH_2CN^+), 3.3 (s, 12 H, N^+CH_3), 3.5 (broad m, 8 H, N^+-$CH_2CCH_2N^+CH_2(C)_2CH_2$).

Ultrafiltrations. All ultrafiltrations were performed in an Amicon Model 202 stirred cell using Amicon membranes: PM10 and YM10 (10000 nominal molecular weight cutoff membranes), PM30 and YM30 (30000 nominal molecular weight cutoff membranes).

General Procedure. The stirred cell was fitted with a membrane and charged with 200 mL of H_2O. This water was then passed through the membrane under 40 psi of N_2 until 20 mL remained. The cell was then emptied, and, if the solvent were other than pure H_2O, the cell would then be filled with that solvent. This solvent was again passed through the membrane until 20 mL remained, and then discarded. At this point, 200 mL of a 0.05% (w/v) solution of the polymer was poured into the cell. This was concentrated to 20 mL as before. This 20 mL, referred to as the retainate, was collected and saved. The procedure was repeated with the remainder of the solution in 200-mL portions. All the retainates from a given solution of polymer were combined, the solvent was evaporated by using a rotary evaporator, and the resulting solid was dried in a vacuum oven at 60 °C. This is the solid referred to as the retained solid.

The combined filtrate was also evaporated and dried. This solid was then redissolved in sufficient solvent to make another 0.05% solution. The above procedure was then repeated by using this "filtrate solution". The percentage of retained solid from this solution was then compared to the percentage retained from the original solution to check for clogging of the membrane. The clogging was evident when the percentage retained from the "filtrate solution" was greater than from the original solution.

33R2 (1b). A 0.5-g sample of 33R2 ionene was dissolved in 1 L of distilled H_2O. The solution was then passed through a YM10 membrane with 0.38 g (76%) of solid retained.

33R4 (1c). A 0.5-g sample of 33R4 ionene was dissolved in 1 L of distilled H_2O. When this was passed through a YM10 membrane, 0.19 g (39%) was isolated from the retainate and 0.18 g (37%) from the filtrate. The solid from the filtrate was dissolved in 360 mL of H_2O and passed through the membrane again; 0.076 g (41%) was retained and 0.103 g (56%) passed into the filtrate.

33R6 (1d). A 0.5-g sample of 33R6 ionene was dissolved in 1 L of 70% aqueous ethanol. This was passed through a YM10 membrane, yielding 0.315 g (63%) from the retainate and 0.175 g (23%) from the filtrate. When the solid from the filtrate was dissolved in 350 mL of 70% aqueous ethanol, 0.089 g (51%) was retained and 0.072 g (41%) passed into the filtrate.

44R2 (1g). A 0.5-g sample of 44R2 ionene was dissolved in 1 L of distilled H_2O and passed through a YM10 membrane; 0.381 g (76%) was isolated from the retainate and 0.095 g (19%) from the filtrate. When this was repeated with 1.0 g in 2 L of distilled H_2O, 0.71 g (71%) was retained.

A 0.3-g sample of 44R2 ionene was dissolved in 600 mL of distilled H_2O and passed through a PM10 membrane; 0.25 g (83%) was isolated from the retainate.

A 0.5-g sample of 44R2 ionene was dissolved in 1 L of distilled H_2O and passed through a YM30 membrane; 0.338 g (67.5%) was retained and 0.117 g (23%) passed into the filtrate.

44R4 (1h). A 0.3-g sample of 44R4 ionene was dissolved in 600 mL of distilled H_2O and passed through a PM10 membrane; 0.26 g (87%) was retained and 0.04 g (13%) passed into the filtrate.

A 0.5-g sample of 44R4 ionene was dissolved in 1 L of distilled H_2O and passed through a YM10 membrane; 0.295 g (59%) was retained and 0.232 g (46%) passed into the filtrate.

44R6. A 0.5-g sample of 44R6 ionene (trial 1) was dissolved in 1 L of distilled H_2O and passed through a YM10 membrane. This gave 0.30 g (60%) retained and 0.215 g (40%) in the filtrate. When the solid from the filtrate was dissolved in 450 mL of distilled H_2O, 0.078 g (39%) was retained and 0.098 g (49%) passed into the filtrate. When this was repeated with 1.0 g in 2 L of H_2O, 0.587 g (59%) was retained.

A 0.5-g sample of 44R6 ionene (trial 2) was dissolved in 1 L of distilled H_2O. When this was passed through a YM10 membrane, 0.35 g (70%) was retained.

A 0.35-g sample of 44R6 ionene (trial 2) was dissolved in 700 mL of distilled H_2O and passed through a YM30 membrane; 0.249 g (71%) was retained.

44R8 (1j). A 0.5-g sample of 44R8 ionene was dissolved in 1 L of 70% aqueous ethanol. This was passed through a YM10 membrane, yielding 0.178 g (36%) retained and 0.286 g (57%) in the filtrate. When the solid from the filtrate was dissolved in 580 mL of 70% aqueous ethanol, 0.108 g (38%) was retained.

66R1 (1k). A 0.3-g sample of 66R1 ionene was dissolved in 600 mL of distilled H_2O. This was passed through a PM10 membrane, yielding 0.27 g (90%) of retained solid.

A 0.5-g sample of 66R1 ionene was dissolved in 1 L of distilled H_2O. This was passed through a PM30 membrane, yielding 0.38 g (76%) of retained solid and 0.047 g (9.5%) in the filtrate.

66R2 (1l). A 0.3-g sample of 66R2 ionene was dissolved in 600 mL of distilled H_2O. This was passed through a PM10 membrane, resulting in 0.244 g (81%) of retained solid.

66R4 (1m). A 0.3-g sample of 66R4 ionene was dissolved in 600 mL of distilled H_2O. This was passed through a PM10 membrane, yielding 0.25 g (83%) of retained solid and 0.05 g (17%) in the filtrate.

66R6 (1n). A 0.375-g sample of 66R6 ionene (trial 4) was dissolved in 750 mL of distilled H_2O. This was passed through a PM10 membrane, resulting in 0.210 g (56%) of retained solid and 0.145 g (39%) in the filtrate. When the solid from the filtrate was dissolved in 300 mL of H_2O and passed back through the membrane, 0.103 g (71%) was retained and 0.036 g (25%) passed into the filtrate.

A 0.5-g sample of 66R6 ionene (trial 6) was dissolved in 1 L of distilled H_2O. This was passed through a YM10 membrane, yielding 0.31 g (62%) from the retainate and 0.18 g (36%) from the filtrate. When the solid from the filtrate was dissolved in 300 mL of H_2O and passed back through the membrane, 0.092 g (51%) was isolated from the retainate and 0.023 g (13%) from the filtrate.

This was repeated twice more, both times using the YM10 membrane. In the first, 0.641 g (64%) was retained from a solution of 1.0 g in 2 L of H_2O. In the second, 0.33 g (66%) was retained from a solution of 0.5 g in 1 L of H_2O.

66R8 (1o). A 0.3-g sample of 66R8 ionene was dissolved in 600 mL of 50% aqueous ethanol. This was passed through a PM10 membrane, giving 0.034 g (11%) from the retainate and 0.246 g (82%) from the filtrate.

A 0.5-g sample of 66R8 ionene was dissolved in 1 L of 50% aqueous ethanol. This was passed through a YM10 membrane, resulting in 0.25 g (50%) in the retainate and 0.248 g (50%) in the filtrate. When the solid from the filtrate was dissolved in 500 mL of 50% aqueous ethanol, 0.092 g (37%) was found in the retainate and 0.144 g (58%) was found in the filtrate.

34R1. A 0.5-g sample of 34R1 ionene was dissolved in 1 L of distilled H_2O. This was passed through a YM10 membrane, yielding 0.327 g (65%) from the retainate and 0.033 g (7%) from the filtrate. Obviously some material was lost; therefore, this was repeated: 0.1 g was dissolved in 200 mL of H_2O. This gave 0.09 g (90%) retained solid and 0.01 g (10%) in the filtrate. When the solid from the original filtrate was dissolved in 67 mL of H_2O and passed through the membrane, 0.02 g (66%) was retained and 0.015 g (45%) passed through.

A 0.05-g sample of 34R1 ionene (trial 2) was dissolved in 1 L of distilled H_2O. This was passed through a YM30 membrane, giving 0.43 g (86%) of retained solid and 0.034 g (7%) in the filtrate.

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Chemistry of Excited Complexes in Copolymers Containing Phenanthrene and *N,N*-Dimethylaniline Moieties. Effects of Chemical Structure on the Intramolecular Exciplex Formation, Its Emission Properties, and Electron Transfer to Dicyanobenzene

Kaoru Iwai,* Keiko Yamamoto, and Fukuo Takemura

Department of Chemistry, Faculty of Science, Nara Women's University, Nara, 630 Japan

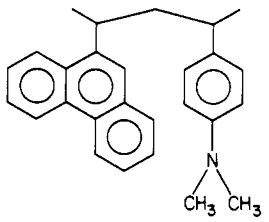
Masaoki Furue and Shun-ichi Nozakura

Department of Macromolecular Science, Faculty of Science, Osaka University, Osaka, 560 Japan. Received May 14, 1984

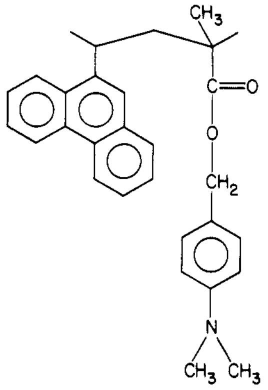
ABSTRACT: The formation and emission properties of intramolecular exciplexes in some vinyl copolymers containing phenanthrene and *N,N*-dimethylaniline moieties were studied. The monomers used were $CH_2{=}CH$-phenanthryl (VPh), $CH_2{=}C(CH_3)COOCH_2$-phenanthryl (PhMMA), $CH_2{=}CH$-DMA (DMAS), and $CH_2{=}C(CH_3)COOCH_2$-DMA (DMAMMA), where Ph and DMA are 9-phenanthryl and 4-(dimethylamino)phenyl groups, respectively. Poly(VPh-*co*-DMAS) was found to exhibit an intense intramolecular exciplex fluorescence, whereas poly(VPh-*co*-DMAMMA), poly(PhMMA-*co*-DMAS), and poly(PhMMA-*co*-DMAMMA) showed only a weak exciplex fluorescence. In poly(VPh-*co*-DMAMMA) the exciplex formation was poor, and in the PhMMA-containing copolymers, the phenanthrene monomer fluorescence was quenched effectively by the DMA chromophores, but the exciplex formed had low fluorescence quantum yields and short fluorescence lifetimes. The electron-transfer reactions in these copolymers + *p*-dicyanobenzene systems were also studied by flash photolysis. The amounts of *p*-dicyanobenzene anion radical detected in these systems decreased in the order poly(VPh-*co*-DMAS) > poly(VPh-*co*-DMAMMA) > poly(PhMMA-*co*-DMAS) ≅ poly(PhMMA-*co*-DMAMMA).

Introduction

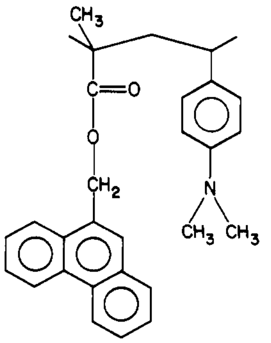
Many investigations on electronic energy migration, electronic energy transfer, and intramolecular excited-complexation form in synthetic polymers have been reported especially over the past decade. Polymers capable of energy migration and exciplex formation would be promising as photosensitizers in the electron-transfer reaction for the storage of light energy. We have studied the formation of intramolecular exciplex and electron transfer from exciplex to electron acceptors in aromatic vinyl copolymer systems.[1-4] Studies on photophysical processes in some phenanthrene-containing vinyl polymers have been reported.[5-7] These polymers showed no distinct low-energy broad-band intramolecular excimer emission but showed electronic energy migration. In a previous paper,[2] the formation of an intramolecular exciplex in 9-vinylphenanthrene-*p*-(dimethylamino)styrene copolymer and the photoinduced electron transfer from the copolymer to *p*-dicyanobenzene were studied. The emission properties and the oxidation potential of the exciplex were studied in comparison with those of a biochromophoric model compound, 1-[4-(dimethylamino)phenyl]-3-(9-phenanthryl)propane.[3,4] In the present paper, we report on the emission properties of vinyl copolymers in which phenanthrene and/or *N,N*-dimethylaniline chromophores were separated from the main chains by an intervening carboxymethylene group ($COOCH_2$). The results are discussed in relation to the relative geometry of the chromophores. The electron-transfer reactions in copolymer + *p*-dicyanobenzene systems were also studied by flash photolysis. The copolymers used in this study are as follows:



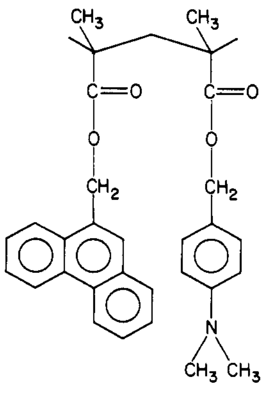
poly(VPh-*co*-DMAS)



poly(VPh-*co*-DMAMMA)



poly(PhMMA-*co*-DMAS)



poly(PhMMA-*co*-DMAMMA)

where DCB = *p*-dicyanobenzene, DMA = *N,N*-di-

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