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Studies of Polymer Compatibility by Nonradiative Energy Transfer

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ABSTRACT: Polymers were prepared carrying fluorescent labels such that nonradiative energy transfer would be efficient over distances of about 2 nm. The emission spectra from blends of two polymers to which donor and acceptor chromophores, respectively, had been attached were then used to characterize the mutual interpenetration of the polymer chains. In blends of poly(methyl methacrylate) with methyl methacrylate–alkyl methacrylate copolymers, the data indicated a gradual change from compatibility to incompatibility. The fluorescence technique was found to be more sensitive to small changes of compatibility than differential scanning calorimetry. Blends of poly(ethyl methacrylate) or poly(propyl methacrylate) with methyl methacrylate–butyl methacrylate copolymers exhibited maximum compatibility when the average length of the copolymer side chains was equal to the length of the side chains in the homopolymer. The range of compositions of styrene–acrylonitrile copolymers which indicated compatibility with poly(methyl methacrylate) by the fluorescence technique was similar to that estimated earlier by other methods.

When a system contains two fluorescing chromophores such that the emission spectrum of the first (the donor) overlaps the absorption spectrum of the second (the acceptor), excitation energy absorbed by the donor can be transferred to the acceptor over considerable distances.[2] The efficiency E of this energy transfer is governed by the relation[2,3]

$$E = R_0^6/(R_0^6 + r^6)$$
$$R_0^6 = (8.8 \times 10^{-25})Jn^{-4}\kappa^2\Phi_D^0 \qquad (1)$$

where r is the distance between donor and acceptor, R_0 is a characteristic distance at which half of the excitation energy is transferred, J is the overlap integral between the emission spectrum of the donor and the absorption spectrum of the acceptor, n is the refractive index, κ^2 is a function of the mutual orientation of the donor and acceptor transition moments, and Φ_D^0 is the fluorescence quantum yield of the donor in the absence of the acceptor.

Nonradiative energy transfer has been used extensively to characterize intramolecular distances in biological macromolecules.[3,4] A number of studies have also been reported dealing with intramolecular energy transfer in synthetic oligomers or polymers,[5] but we know of no previous study dealing with intermolecular energy transfer between two polymers labeled with donor and acceptor chromophores, respectively. In the present investigation we used this phenomenon as an experimental tool to study the compatibility of mixed chromophore-labeled polymers in bulk. It was expected that phase separation would lead to a large increase in the distances between the donors and the acceptors, reducing substantially the efficiency of energy transfer.

Experimental Section

Monomer and Analogue Preparations. 1-(2-Anthryl)ethanol was prepared as described by Etienne et al.[6] (mp 164 °C (lit.[7] mp 162–163 °C)) and 1-(2-naphthyl)ethanol (mp 76 °C (lit.[8] mp 71–72 °C)) was obtained by an analogous procedure from 2-acetylnaphthalene (Pfaltz and Bauer) recrystallized from ethanol (mp 56 °C (lit.[9] mp 56 °C)). 9-Anthrylmethanol was obtained from the Aldrich Chemical Co. *N*-(2-Hydroxyethyl)carbazole (mp 82–83 °C (lit.[10] mp 82–83 °C)) was prepared from carbazole and ethylene oxide in the presence of sodium hydroxide by the procedure of Lopatinskii et al.[10] These alcohols were converted by methacryloyl chloride to 1-(2-anthryl)ethyl methacrylate (AEMA) (mp 161 °C (lit.[7] mp 161 °C)), 1-(2-naphthyl)ethyl methacrylate (NEMA) (mp 52 °C), 9-anthrylmethyl methacrylate (mp 86–87 °C) (AMMA) and 2-(*N*-carbazolyl)ethyl methacrylate (CEMA) (mp 82.5–4 °C). The corresponding acetates, used as low molecular weight analogues of the fluorescing residues in the copolymers, were 1-(2-anthryl)ethyl acetate (AEA) (mp 140–141 °C (lit.[7] mp 140–141 °C)), 1-(2-naphthyl)ethyl acetate (NEA) (liquid at room temperature), 9-anthrylmethyl acetate (AMA) (mp 110–111 °C) and 2-(*N*-carbazolyl)ethyl acetate (CEA) (mp 69–71 °C).

Polymerization and Polymer Characterization. Polymerizations were carried to low conversion at 60 °C, using azobis(isobutyronitrile) initiator (0.1% on the weight of the monomer). The concentration of the chromophore-carrying methacrylate residues in the polymers was determined assuming that their extinction coefficients were the same as those of the corresponding acetates (cf. Table I). In the copolymerization of methyl methacrylate (MMA) with AEMA and NEMA, no significant difference was found in the composition of the polymer and monomer mixture, and it was assumed that terpolymers containing two alkyl methacrylates also contained their residues in the same proportion as the monomer mixture from which they were derived. The composition of styrene–acrylonitrile copolymers was determined by IR spectroscopy, using methylene chloride solutions and the absorbance at 2240 cm^{-1} as a measure of the concentration of nitrile groups, with isobutyronitrile as a reference standard. Molecular weights of the polymers were characterized by intrinsic viscosity (specified in the legends to the graphs in units of dL/g).

Film Casting. Films were cast from 10% tetrahydrofuran or methylene chloride solutions containing equal concentrations of two polymers carrying donor and acceptor fluorescent labels, respectively, onto Teflon plates after removal of dissolved gases by exposure of the solution to a reduced pressure. The solvent was allowed to evaporate slowly for 2 days at room temperature in a nitrogen atmosphere and the films were then dried for a day in a vacuum oven at 50 °C. They were stored under vacuum up to the time of fluorescence measurements to avoid fluorescence quenching by oxygen. In the study of blends of poly(methyl methacrylate) with alkyl methacrylate copolymers, the film thickness was held to 0.035 ± 0.005 mm. In later experiments, a film thickness of 0.015 ± 0.005 mm was used.

Fluorescence Measurements. Emission spectra were recorded on a Hitachi-Elmer MPF-2A spectrophotometer equipped with a 150 W xenon lamp, a R 106 photomultiplier, and a PQD recorder. For the determination of reflectance fluorescence spectra, films were mounted between quartz plates with the exciting beam at 60° and the observation of the emission at 30° to the sample surface.

Glass Transition Measurements. The glass transitions of polymer films were determined by using a DuPont thermal analyzer 900 modified with a 900693 rebuilt DSC cell. The polymer sample and an empty reference pan were heated at a rate of 10 °C/min up to 140 °C. The sample was then rapidly quenched in dry ice and the thermal behavior was recorded from 0 to 130 °C under nitrogen.

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Table I
Spectroscopic Data for Donor-Acceptor Pairs

compd	λ_{ex}, nm	λ_{max}, nm	$10^3\epsilon_{ex}$, M^{-1} cm^{-1}	$10^3\epsilon_{max}$, M^{-1} cm^{-1}	λ_{em}, nm	$10^{15}J$,[12] cm^6 mol^{-1}	Φ_D^0 [13]	R_0, nm
NEA	276	276	5.2	5.2	336	5.13	0.13	1.9-2.0
AEA	276	357	1.16	6.5	408			
CEA	296	296	15.4	15.4	347	9.07	0.69	2.7-2.9
AMA	296	386	0.60	8.8	413			

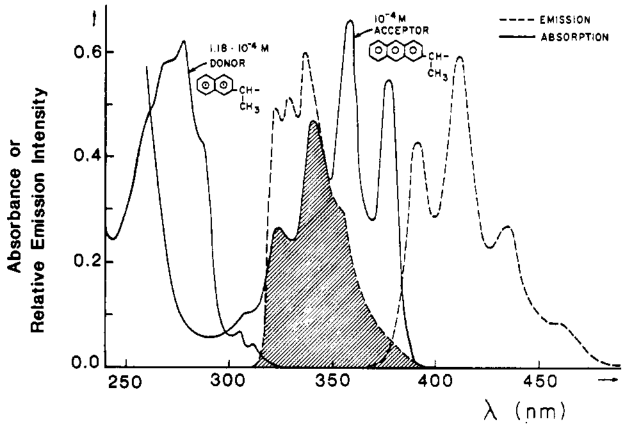


Figure 1. Absorption and emission spectra of NEA and AEA. The overlap integral is crosshatched.

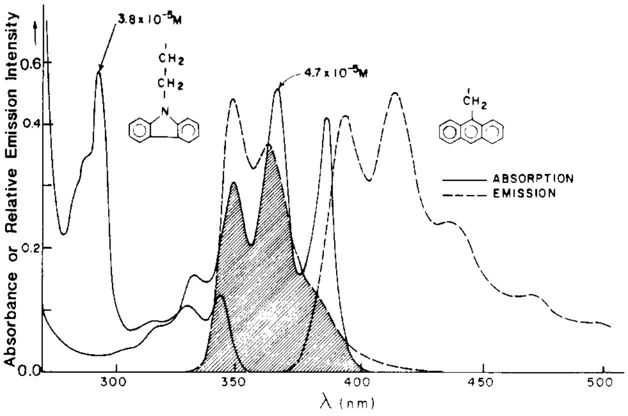
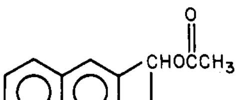


Figure 2. Absorption and emission spectra of CEA and AMA. The overlap integral is crosshatched.

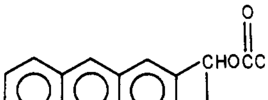
Results and Discussion

Characterization of Chromophore Labels. For chromophore labels appended to polymers for studies of compatibility by nonradiative energy transfer, the product of the overlap integral J between the donor emission and the acceptor absorption spectrum and of the donor fluorescence quantum yield Φ_D^0 must be sufficiently large to yield a characteristic distance, R_0, for energy transfer not less than about 2 nm. In the present study two methacrylate derivative pairs carrying donor and acceptor chromophores were employed as comonomers to introduce the labels into the polymers. The corresponding acetates, with structures given below, were used to determine their

donor-acceptor pair I

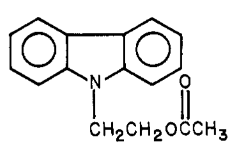


NEA

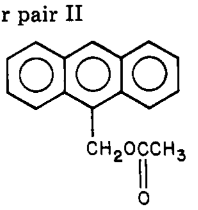


AEA

donor-acceptor pair II



CEA



AMA

spectroscopic characteristics. These are given in Table I, which lists the excitation wavelength, λ_{ex}, with the molar extinction coefficients of the donor and of the acceptor, ϵ_{ex} and ϵ_{max}, at the excitation wavelengths and the absorption maximum, respectively, wavelength λ_{em} of the emission maxima of donor and acceptor, Φ_D^0, J, and R_0. A value of $\kappa^2 = 0.476$ (corresponding to a random orientation of donor and acceptor in a rigid medium[11]) and n values ranging from 1.48 for poly(butyl methacrylate) and $n = 1.59$, for polystyrene, were used in calculating R_0. The absorption and emission spectra of the two donor-acceptor pairs are shown in Figures 1 and 2.

In the initial study, involving mixtures of poly(methyl methacrylate) (PMMA) with methyl methacrylate-ethyl methacrylate (MMA-EMA) and methyl methacrylate-butyl methacrylate (MMA-BMA) copolymers, the comonomers NEMA and AEMA were employed to introduce the fluorescent labels. In later investigations, we used for this purpose the donor-acceptor pair CEMA-AMMA, which is characterized by a larger $J\Phi_D^0$[12,13] and has the advantage that it can be excited at 296 nm, a wavelength at which styrene copolymers have no significant absorption.

Energy Transfer between PMMA and Methyl Methacrylate Copolymers.[14] In a blend containing a mixture of a donor-labeled polymer and an acceptor-labeled polymer, energy transfer would be expected to be favored if the two polymeric species can freely interpenetrate one another in a single phase. On the other hand, if the system separates into two phases, energy transfer will only be possible in the neighborhood of the phase boundary. Thus, the emission spectrum from such a blend should contain information concerning the compatibility of the two polymeric species. To evaluate the utility of this method, we determined the ratio I_N/I_A of the emission intensities at the λ_{em} wavelengths of the naphthyl and anthryl groups in films containing equal weights of a terpolymer of methyl methacrylate with ethyl or butyl methacrylate and 1.2 wt % of NEMA and a copolymer of methyl methacrylate with 1.4 wt % of AEMA. The results plotted in Figure 3 show that this ratio increases, corresponding to a decreasing energy transfer, as the ethyl or butyl methacrylate content of the copolymer is increased but levels off to a constant value for blends in which the copolymer contains less than 60 mol % of methyl methacrylate. The fluorescence spectra thus reflect the decreasing compatibility of the two components of the blend, leading eventually to a two-phase system. Three features of the results deserve special notice.

(1) The data suggest that the transition from compatibility to incompatibility occurs gradually over a broad range of the copolymer composition. This is in sharp contrast to results obtained by Fried et al.[15] in a differential

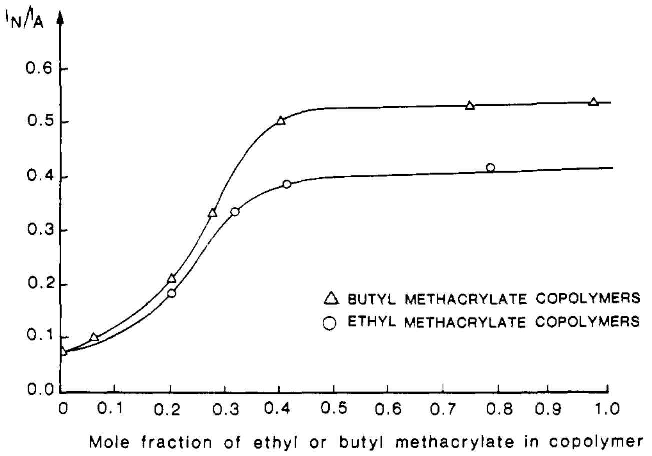


Figure 3. Ratio of donor and acceptor fluorescence intensities in films containing equal weights of donor-labeled methyl methacrylate–ethyl methacrylate or methyl methacrylate–butyl methacrylate copolymers ($[\eta]_{25}$ = 2.2–2.4 in dioxane) and acceptor-labeled poly(methyl methacrylate) ($[\eta]$ = 2.0 in dioxane).

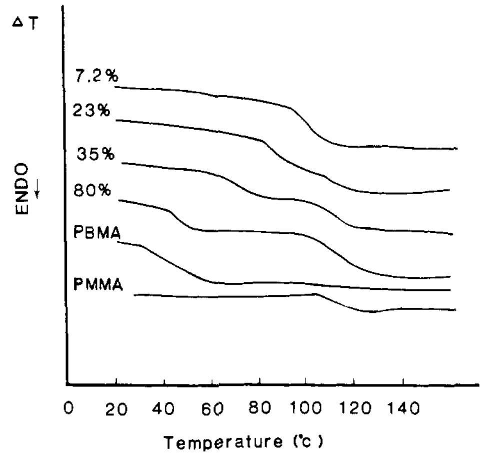


Figure 4. DSC traces of poly(methyl methacrylate), poly(butyl methacrylate), and mixtures of equal weights of PMMA with methyl methacrylate–butyl methacrylate copolymers. The numbers specify the mole percent of butyl methacrylate residues in the copolymer.

scanning calorimeter (DSC) study of blends of poly(2,6-dimethyl-1,4-phenylene oxide) with styrene-4-chlorostyrene copolymers. This study indicated that the transition from a one-phase to a two-phase behavior occurs sharply at a critical concentration of the copolymer. As will be shown later, glass transition phenomena, as reflected in the calorimetric behavior of polymer blends, are much less sensitive than energy transfer between polymer-bound chromophore label in revealing the mutual interpenetration of polymer chains.

(2) When the solutions of NEA and AEA with the same optical density at the excitation wavelength of 276 nm were irradiated, the ratio of the fluorescence intensities at 336 and 408 nm was 0.87. Since the ratio of the molar extinction coefficients of these species at 276 nm is 4.48 and the ratio of the molar concentration of donors and acceptors in the polymer blend is 1.04, a ratio I_N/I_A = 4.7 would be expected in the absence of energy transfer. It may be seen on Figure 3 that I_N/I_A values actually observed in the plateau region are lower by an order of magnitude. This suggests that we must be dealing in the two-phase systems with extremely small phase domains.

(3) It was expected that incompatibility with PMMA would require a larger content of ethyl methacrylate than butyl methacrylate in the copolymer. This was not observed. Figure 3 shows that the plateau region is attained at the same comonomer content in the two systems. The somewhat larger energy transfer characterizing the two-phase systems containing ethyl methacrylate copolymers may reflect a smaller interfacial energy leading to an increased interfacial area.

DSC Studies of Blends of PMMA with Methyl Methacrylate Copolymers. DSC traces of PMMA, poly(butyl methacrylate), and blends of PMMA with methyl methacrylate–butyl methacrylate (BMA) copolymers are shown on Figure 4. The blends containing copolymers with 80 and 35 mol % of BMA reveal two glass transitions. The double T_g is less evident in the blend in which the copolymer contains 23 mol % of BMA and is totally absent in a blend with a copolymer containing 7.2 mol % of BMA. Thus, DSC is unable to reveal the less intimate mixing which results when two components of a blend differ only slightly in their composition. Also, DSC results would class a blend as containing two phases before the plateau region is reached in the fluorescence characteristics of the chromophore labeled polymer blends. Similar conclusions were arrived at in DSC studies of blends of PMMA with methyl methacrylate–ethyl methacrylate copolymers and a comparison with fluorescence data on these systems.

Past studies have shown that measurements of dynamic mechanical properties are more sensitive to the separation of polymer blends into two phases than DSC measurements[16] and that electron microscopy can detect even smaller domains in a two-phase system.[17] It would be most desirable to compare in the future results obtained by these two techniques with those obtainable by fluorimetry.

Energy Transfer between Poly(ethyl methacrylate) or Poly(propyl methacrylate) with Methyl Methacrylate–Butyl Methacrylate Copolymers. In the absence of specific molecular interactions such as hydrogen bonding, it would be expected that a matching of cohesive energy densities would be the appropriate condition necessary to arrive at compatible polymer blends. A particularly simple system on which this assumption can be tested would consist of an alkyl methacrylate homopolymer and alkyl methacrylate copolymers. If the cohesive energy is the sum of contributions from chemical groups constituting a polymer, as has been demonstrated by a number of investigators,[18] then a methacrylate homopolymer and a methacrylate copolymer should be miscible if the mean length of the copolymer side chains matches the length of the homopolymer side chains. Fluorescence data obtained with blends of poly(ethyl methacrylate) or poly(propyl methacrylate) with methyl methacrylate–butyl methacrylate copolymers are plotted in Figure 5. It may be seen that the ratio of the emission intensities of the CEMA and AMMA residues, I_C/I_A, passes through a minimum with mole fractions of 1/3 and 2/3 butyl methacrylate in the copolymers when they are blended with poly(ethyl methacrylate) and poly(propyl methacrylate), respectively. This is precisely the point of maximum compatibility predicted from cohesive energy density considerations.

Energy Transfer between Poly(methyl methacrylate) and Styrene–Acrylonitrile Copolymers (S–AN). This system is of special interest since compatibilities have previously been studied by a number of techniques.[19] Solutions of styrene–acrylonitrile copolymers in poly(methyl methacrylate) have also been investigated by neutron scattering.[20] Plots of I_C/I_A for blends of PMMA with S–AN of varying composition are shown in Figure 6 for two PMMA samples of different molecular weight. As would be expected, an increasing molecular weight renders compatibility more difficult. Nevertheless,

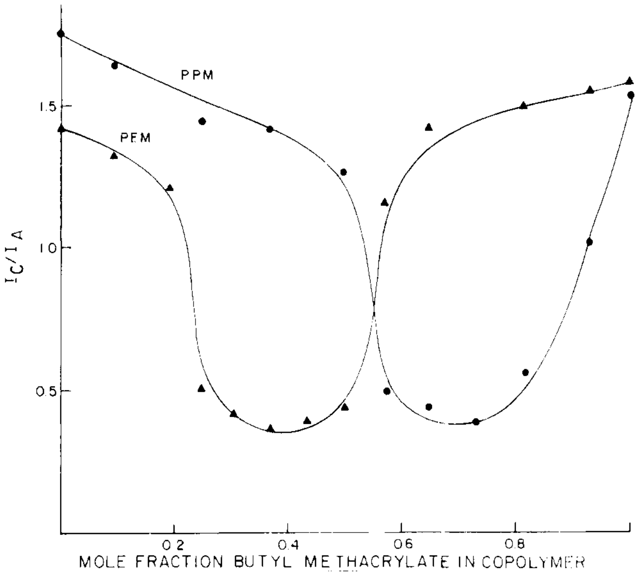


Figure 5. Ratio of donor and acceptor fluorescence intensities in films containing equal weights of poly(ethyl methacrylate) (PEM, $[\eta]_{30} = 1.24$) or poly(propyl methacrylate) (PPM, $[\eta]_{30} = 1.35$) labeled with 1.1 wt % of AMMA and a methyl methacrylate–butyl methacrylate copolymer labeled with 0.8 wt % of CEMA ($[\eta]_{30} = 0.6$–0.8 in benzene).

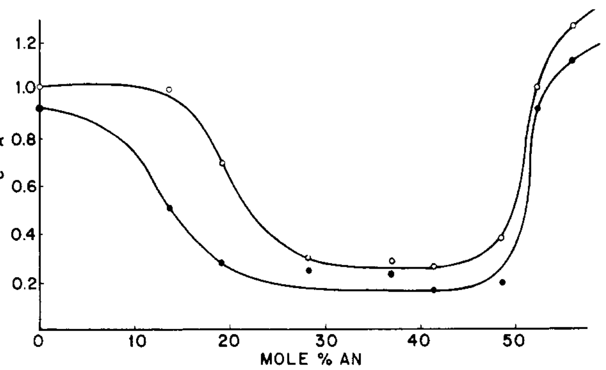


Figure 6. Ratio of donor and acceptor fluorescence intensities in films containing equal weights of styrene–acrylonitrile copolymers labeled with 1.45 wt % of CEMA and poly(methyl methacrylate) labeled with AMMA: (○) $[\eta]_{PMMA} = 1.06$, 0.91 wt % AMMA; (●) $[\eta]_{PMMA} = 0.18$, 1.00 wt % AMMA. The $[\eta]$ were measured in benzene at 25 °C; for the copolymers they increased with increasing acrylonitrile content from 0.51 to 0.97.

it is surprising that the I_C/I_A minimum is distinctly higher with the longer PMMA, suggesting that the interpenetration with S–AN is somehow less perfect even when the compatibility of the two materials has been optimized.[21] It should also be noted that the range of compatibility which lies according to Stein et al.[19] between 16 and 42 mol % of acrylonitrile in the copolymer is located more narrowly by the fluorescence technique.

Concluding Remarks. This investigation has shown that energy transfer between polymers labeled with donor and acceptor chromophores provides a powerful tool for the study of polymer compatibility. It should be noted, however, that changes in the ratio of donor and acceptor fluorescence intensity do not define uniquely the distribution of the macromolecular species. This ratio should, in fact, be sensitive both to the size and the geometry of phase domains.

One of the most striking features of our results is the apparently gradual transition from a two-phase to a one-phase behavior. At least four different interpretations for such a gradual change can be thought of: (1) Since the polymers are polydisperse, incompatibility may gradually extend to lower molecular weight fractions. (2) The phase boundary may not be sharp, and the depth to which polymers contained in one phase penetrate into the other may gradually decrease. "Fuzzy" phase boundaries between two polymers have, in fact, been observed both by electron microscopy[22] and phase-contrast microscopy.[23] (3) A gradually decreasing energy transfer may reflect a decrease in the interfacial area due to an increase in the interfacial energy. (4) Composition fluctuation may appear on a microscopic scale, although no phase separation is involved. Such phenomena were observed by electron microscopy[24] and by pulsed NMR[25] in blends which appeared homogeneous by the usual diagnostic criteria. Although such phenomena are revealed by these methods, the technique we have used recommends itself by its great experimental simplicity.

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(12) These values were obtained without correcting the experimental emission spectra for the wavelength dependence of the fluorimeter sensitivity. It was confirmed that the error thus introduced is minor since the overlap integral is largely determined by the emission intensity of the donor in a narrow spectral range. It may be noted that the J value for the CEA–AMA pair is identical with that given by I. B. Berlman for the N-methylcarbazole–9-methylanthracene pair ("Energy Transfer Parameters of Aromatic Molecules", Academic Press, New York, 1973, p 208).

(13) The $\Phi_D{}^0$ values were estimated by comparing the areas under the emission spectra of NEA and CEA with those of 2-methylnaphthalene and carbazole, respectively, and using for the $\Phi_D{}^0$ of the latter two compounds the values given by I. B. Berlman, "Handbook of Fluorescence Spectra of Aromatic

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Synthesis and Investigation of Macrocyclic Polystyrene[‡]

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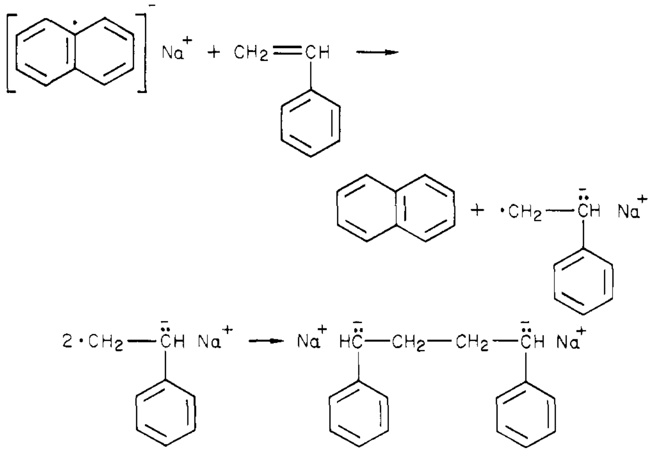
ABSTRACT: Macrocyclic polystyrene samples (30 < DP < 250) with narrow molecular weight distribution have been prepared by living bifunctional anionic polymerization and by coupling with α,α'-dichloro-*p*-xylene. The polymers have been investigated by gel permeation chromatography and viscosity measurements. The GPC data of both cyclic and acyclic polymers fulfill the Benoit relationship. The ratio of the intrinsic viscosity of ring and linear polymer chains was found to be close to 0.65 in cyclohexane at 34.5 °C. In toluene at 25 °C it is a function of the molecular weight ($0.56 < [\eta]_r/[\eta]_l < 0.76$).

A broad variety of circular DNA has been observed in the past,[1-3] proving the high biological importance of ring-shaped molecules.

On the other hand a number of theoretical studies have appeared treating the hydrodynamic properties of cyclic macromolecules in comparison with linear molecules of the same molecular weight.

Reports on synthetic cyclic polymers occur only sporadically in the literature. Semlyen et al.[4] described the preparation and characterization of cyclic poly(dimethylsiloxane) $[(CH_3)_2SiO]_x$ and Jones[5] reported on cyclics in styrene–dimethylsiloxane block copolymers.

In the present paper we describe a method for the preparation of cyclic polystyrene by anionic polymerization using sodium naphthalene as an initiator[6] which generates a bifunctional "living" chain and α,α'-dichloro-*p*-xylene as a bifunctional terminating agent. Linear and cyclic molecules were separated by fractionation after reaction of the linear molecules having chlorine end groups with high molecular weight living polystyrene.



The cyclic polymers with narrow (nearly Poisson) molecular weight distribution have been characterized by gel permeation chromatography and by viscosity.

Experimental Section

1. Materials. Inert gases (N_2, Ar) were purified by passing them through columns filled with Al_2O_3 as a support for metallic potassium and bubbling them through a solution of α-methylstyrylsodium.

Tetrahydropyran was refluxed over K and fractionated. Then it was stored over potassium benzophenone ketyl and distilled off before use.

Naphthalene was purified by sublimation.

α,α'-Dichloro-*p*-xylene (Schuchardt, Munich) was recrystallized from ethanol and sublimated in N_2 atmosphere. The melting point of the pure product was 100 °C.

Styrene was purified in the usual manner. Before use it was distilled from $LiAlH_4$.

2. Preparation of Polystyrene and Cyclization. The apparatus for polymerization and cyclization reactions is shown in Figure 1. It was heated in vacuo with a flame and then filled with Ar. From the 2-L flask A containing tetrahydropyran (THP) as a solvent and the tetrameric dianion of α-methylstyrene with Na^+ as the gegenion, THP was distilled into the 2-L flask B in vacuo. Via tube k all flasks can be filled with pure THP. In flask C the initiator, sodium naphthalene, was prepared in THP. From flask F containing styrene and $LiAlH_4$, styrene was distilled in vacuo into flask E. In flask D the polymerization of styrene (0.07 mol, dissolved in 500 mL of THP) initiated by sodium naphthalene (the amount calculated to achieve a certain degree of polymerization) took place. Half of the living solution was taken off via tube l and protonated by means of methanol to yield an acyclic polystyrene sample. The other half was added dropwise and simultaneously with an equimolar amount of α,α'-dichloro-*p*-xylene dissolved in 250 mL of THP (flask H) to 1 L of pure THP (flask G) where cyclization took place. At the end of the reaction an excess of dichloro compound was added to provide all residual open chain species to carry Cl end groups.

3. Separation of Macrocycles and Acyclic Material. The material obtained after the cyclization reaction was freeze-dried, dissolved in 100 mL of THP, and reacted with high molecular weight (50 000 < M < 200 000) living polystyrene prepared with a bifunctional initiator in THP solution which was added dropwise

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[†] Part of her Ph.D. Thesis.

[‡] Dedicated to Professor P. J. Flory on the occasion of his 70th birthday with very best wishes.

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