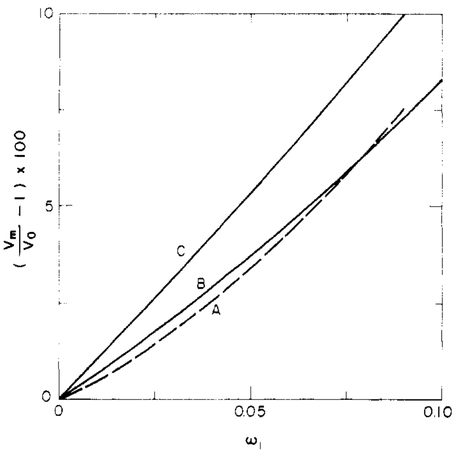

Figure 1. Volumetric behavior of glassy polycarbonate–carbon dioxide system at 35 °C: (A) experimental data of Fleming and Koros;[1] (B) prediction of eq 3 with $\hat{V}_1{}^0 = 0.85$ cm^3/g; (C) prediction of eq 2 with $\hat{V}_1{}^0 = 0.85$ cm^3/g.

which are in reasonably good agreement with the experimental data. This agreement is obtained even though the sample preparation histories for the theory and experiment are different and even though there may be some error introduced by the assumption that the volumetric behavior of the carbon dioxide is described by a constant specific volume, $\hat{V}_1{}^0$. We believe it is fair to conclude that the present approach provides a reasonable alternative to the dual-mode sorption model. However, no firm conclusions about the applicability of the two models can be made for the description of the volumetric behavior of the glassy polycarbonate–carbon dioxide system until a definitive value for $\hat{V}_1{}^0$ is available.

We conclude by commenting on the basic assumptions and possible limitations of the proposed theory for volumetric behavior in glassy polymer–penetrant systems. As noted above, the model of volumetric behavior is based on the premise that the molecular structure of the system is modified as a penetrant or antiplasticizer is added to the glassy polymer. The glassy polymer is in a nonequilibrium liquid configuration with extra hole free volume which is effectively frozen into the polymer. As a diluent is added to the polymer, there is a change in molecular structure in the sense that the system generally tends toward an equilibrium liquid configuration. The addition of diluent essentially leads to an eventual elimination of the extra hole free volume for the system. The premise that the structure of a glassy polymer changes as diluent is added is implied, for example, in a paper by Wyzgoski and Yeh.[5]

The determination of the exact nature of this volume relaxation involves the solution of a complex problem in volume viscoelasticity. In this and a previous paper,[2] the need to determine a solution to this complex problem is circumvented by assuming that the samples for the polymer–penetrant system are prepared in a simple manner. Although the predictions of the model are thus restricted, strictly speaking, to samples prepared in this manner, it is evident from the results presented here and in an earlier paper[2] that the above theory can also be used to provide reasonably good predictions for volumetric behavior for other sample preparation histories. It, of course, will not be possible to obtain useful predictions for all sample preparation histories by the above simple approach, but that does not necessarily mean that the premise that the addition of diluent leads to a modification in the molecular structure is incorrect. In such cases, a solution of a problem in volume viscoelasticity will have to be obtained to predict the volumetric behavior.

Finally, we note that the prediction of volumetric behavior for glassy polymer–penetrant systems is somewhat more difficult when the penetrant is a gas rather than a liquid at the temperature of interest, since a good estimate for $\hat{V}_1{}^0$ is generally not available for gaseous penetrants. Since both the present model and the model of Fleming and Koros[1] require a good estimate for $\hat{V}_1{}^0$, there is clearly no advantage of one model over the other in this regard.

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Registry No. CO_2, 124-38-9.

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Electron Transport and Carrier Generation Characteristics of Poly[2-((3,5-dinitrobenzoyl)oxy)ethyl methacrylate]

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ABSTRACT: A methacrylate containing a 3,5-dinitrobenzoyl group (DNB), as an aromatic electron acceptor, was synthesized and polymerized. A radically initiated polymerization of this monomer, 2-((3,5-dinitrobenzoyl)oxy)ethyl methacrylate, gave a polymer with $\bar{M}_w$ of 2.1×10^4. Electron transport characteristics of the polymer were investigated by the time-of-flight technique, revealing that this polymer has photoconductivity. The electron drift mobility for the polymer was determined to be ca. 1.4×10^{-6} cm^2/(V s) at 10^5 V/cm. The apparent carrier injection efficiency of the polymer from a-Se and the carrier generation efficiency of a charge transfer complex of the polymer with poly(2-*N*-carbazolylethyl acrylate) were studied by the photodischarge technique.

Introduction

Electron-acceptor polymers are of interest from standpoints of an electronic property of polymers with an application to electronic devices. Although there are many reports on such electron-donor polymers as poly(*N*-vinylcarbazole), few studies about electronic properties of electron-acceptor polymers have been reported. For instance, the polymers containing 2,4,7-trinitro-9-fluorenone

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(TNF) were reported.[1,2] However, the polymers had low molecular weights, probably because the chromophore with a strong electron-withdrawing property prevented the monomer from generating high molecular weight polymers. Thus, their electronic properties have not been investigated in detail.

3,5-Dinitrobenzoyl group (DNB) has a lower electron affinity than the TNF group. Radical polymerization of monomers containing DNB have given relatively high molecular weight polymers. These monomers have been copolymerized with donor monomers, e.g., *N*-vinylcarbazole.[3] Although photocurrents of the copolymer were investigated, it is assumed that the photocurrent is attributed mainly to positive holes originating from carbazole groups. No investigation has dealt with the electronic properties of pure DNB polymers.

In this paper, we report the synthesis of high molecular weight poly[2-((3,5-dinitrobenzoyl)oxy)ethyl methacrylate] and a electron drift mobility of the polymethacrylate which has been measured by time-of-flight technique. In addition, we report carrier generation characteristics of a polymer blend containing poly[((3,5-dinitrobenzoyl)oxy)ethyl methacrylate] as an acceptor polymer and poly(2-*N*-carbazolylethyl acrylate) as a donor polymer. In the latter study, a photodischarge technique is used for the photoconductivity measurement.

Experimental Section

Syntheses and Polymerization of Monomers. 2-((3,5-Dinitrobenzoyl)oxy)ethyl methacrylate and acrylate were synthesized by the reaction of 3,5-dinitrobenzoyl chloride with 2-hydroxyethyl methacrylate and acrylate, respectively.[4] Ethyl 3,5-dinitrobenzoate (EtDNB), as a low molecular weight model compound, was also synthesized by a similar procedure. The monomer structure was determined by ^1H NMR spectroscopy.

The monomer (0.5 g) was polymerized by using azobis(isobutyronitrile) (5 mg) as an initiator and dry benzene (5 mL) as solvent under reduced pressure at 60 °C for 48 h. The resulting polymer was purified three times by reprecipitation with tetrahydrofuran–methanol system and dried under vacuum at 40 °C for 24 h.

Measurement. Sample Films for Measurements of Electronic Properties. For the photodischarge measurement, the sample film with thickness of ca. 4 μm was made by applying the THF solution of the polymer on an aluminum substrate, followed by vapor-depositing a-Se layer on the dried film. For the time-of-flight measurement, the sample film with thickness of ca. 15 μm was made by a similar procedure and was vapor-deposited with Se as a carrier generation layer and gold as an electrode.

Apparatus. The molecular weight of the polymer was determined by GPC (elution, THF; standard, polystyrene). The time-of-flight measurement was carried out by using a 8-μs Xe lamp. The transient current was measured by using a National VP-5730A digital storage oscilloscope. The current–time curve was analyzed by using a NEC PC-9801 VM personal computer. The photodischarge measurement was carried out by using a deuterium lamp. The charged sample was irradiated with a monochromatic light of low intensity, and the photodischarge behavior was measured by using a Monroe electronics Model 244 electrostatic voltmeter and the digital storage oscilloscope. The carrier generation efficiency was calculated from initial 5% discharge. The UV spectrum of a THF solution of the polymer and the IR spectrum of the polymer in the KBr pellet were measured by using a Hitachi 557 double-beam spectrophotometer and a Hitachi 260-10 infrared spectrophotometer, respectively.

Result and Discussion

Polymerization and Polymer Structure. The methacrylate was polymerized with a radical initiator to a polymer (PDNBM) with $\bar{M}_w$ of 2.1×10^4 in 67% yield, while the acrylate gave a polymer (PDNBA) with $\bar{M}_w$ of 2×10^3 in 12% yield. In general, polymerization of a methacrylate monomer has a tendency to be polymerized into a higher molecular weight polymer than an acrylate monomer with the same ester group, probably because a radical from the methacrylate monomer is more stable than that from the acrylate monomer. In a radical polymerization of the monomers containing the DNB group, a radical can easily react with both C=C double bond and nitro group, and so propagation reaction is to a large extent prevented. However, the result of polymerizations revealed that the methacrylate has a higher reactivity than the acrylate.

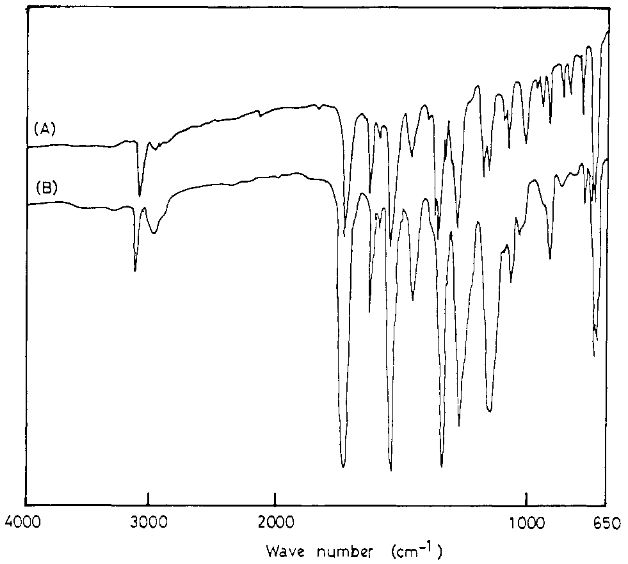

Figure 1. IR spectrum of ethyl 3,5-dinitrobenzoate (A) and poly[2-((3,5-dinitrobenzoyl)oxy)ethyl methacrylate] (B).

IR spectrum of PDNBM is compared with that of EtDNB in Figure 1. Little difference was observed between the two spectra. Both spectra had an absorption due to carbonyl groups around 1720 cm^{-1} and the nitro group absorptions around 1560 and 1350 cm^{-1}. No absorption, which might be derived from polymer branches caused by the chain transfer reaction between the nitro group and the growing polymer radical, was observed around 1610–1680 cm^{-1} in the spectra of PDNBM. This indicates that the chain transfer reaction did not occur to a significant extent during polymerization of the methacrylate, and consequently the polymer had an almost linear structure. Accordingly, there was no irregular structure such as a branch at a nitro group which might become a trap in charge transport.

The polymethacrylate had a good film forming property. On the other hand, film of the polyacrylate could not be formed, probably because of its low molecular weight.

Electron Drift Mobility. By time-of-flight measurement, the photocurrent was observed when positive voltage was applied on aluminum side of the sandwich cell. This indicates that the carrier in PDNBM is an electron. Since the curve showing relation between transient current and time, which was obtained by the time-of-flight measurement, was very dispersive, the transient time was determined from the shoulder in the bilogarithm plot of current and time. After the sample film was kept in air, the curve became more dispersive and the transient time could not be determined even from the bilogarithm plot. The shoulder reappeared after the film was heated at 50 °C for 5 min. Therefore, the values of transient time at the same condition were measured several times by using both original and heated films and they were averaged. The scattering of values was within 10%. This suggests that protonation of the nitro group might take place in moisture

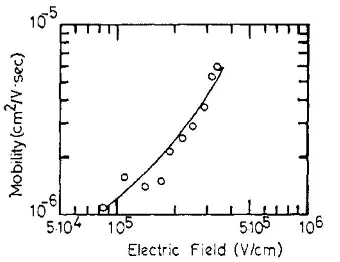

Figure 2. Field dependence of room-temperature electron drift mobility for poly[2-((3,5-dinitrobenzoyl)oxy)ethyl methacrylate] at 20 °C; film thickness ca. 10–18 μm.

to cause trapping of carriers, as was pointed out by previous reports.

Field dependence of the electron mobility for PDNBM is depicted in Figure 2. The mobility for PDNBM was determined to be ca. 1.4×10^{-6} cm²/(V s) at 10^5 V/cm. This value was lower than the mobility (5×10^{-5} cm²/(V s) at 10^5 V/cm) determined for an amorphous 2,4,7-trinitro-9-fluorenone (TNF) film,[6] possibly because the concentration of chromophore in PDNBM is lower than that in the neat film of TNF.

However, it was one order of magnitude larger than the value (2.8×10^{-8} cm²/(V s) at 10^5 V/cm) for poly(2-ethylmethacryl 4,5,7-trinitro-9-fluorenone-2-carboxylate).[2] Two reasons may account for this result. (1) Since electron affinity of the DNB group is lower than that of the TNF–carboxylate group, an electron hops more easily in the DNB system than in the TNF–carboxylate system. (2) According to Bässler's study, the carrier transport occurs by hopping across sites with a Gaussian density-of-sites distribution.

By use of Bässler's model, the field and temperature dependence of the carrier mobility is described as[6]

$$\mu = \mu_0 \exp[-(T_0/T)^2] \exp(E/E_0)$$

where

$$T_0 = \kappa\sigma$$

$$E_0 = (\sigma/2Be\rho)(T/T_0)$$

μ_0 is the mobility in a similar system without disorder, $\kappa = 7400$ K/eV, σ is the width of a Gaussian sites state energy distribution, $B = {}^1/_6$, and ρ is the average separation between sites. High molecular motion of the chromophore decreases the σ value to afford high carrier mobility.[8] Since the DNB group is smaller in size than TNF carboxyl group, the molecular motion of DNB group must be higher than that of TNF carboxyl group.

Carrier Generation Properties. Although the UV-absorption maximum of PDNBM existed around 280 nm, the photogeneration of electron was not observed by the irradiation of this UV light (250–600 nm). Because low photocarrier generation efficiency (less than 5×10^{-5}) could not be determined by our instruments, PDNBM probably had no or very low photocarrier generation properties. It is assumed that in the case of PVK, the adsorbed oxygen plays as an acceptor, and so the photocurrent is generated by excitation of the carbazole group with light irradiation.[8] On the other hand, in the case of PDNBM, no sensitizer exists in atmosphere and no photocurrent is generated.

Electron Injection from a-Se. Electron injection efficiency of the PDNBM from a-Se layer is exhibited in Figure 3. At 10^5 V/cm, the efficiency was determined to be 2×10^{-2}. This value was in the same order as that of the hole injection efficiency of the poly(*N*-vinylcarbazole) (PVK) film from a-Se.[9] In the case of hole injection, the energy barrier does not exist between a-Se and PVK in the system.[10] Since the number of electrons generated in a-Se is the same as that of holes, it is reasonable to assume that little energy barrier against electron injection also exists between a-Se layer and the polymer film.

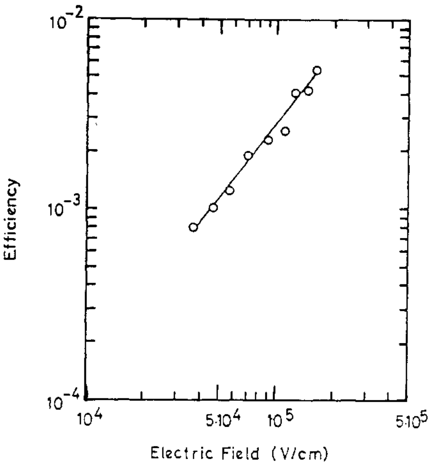

Figure 3. Apparent electron injection efficiency of poly[2-((3,5-dinitrobenzoyl)oxy)ethyl methacrylate] from a-Se.

Charge-Transfer Complex Behavior. Polymeric donors have shown polymer chain effects on complex formation, which are thought to be due to higher order complexes.[2] In the UV spectroscopy, these effects have been observed a bathochromic shift of λ_{max} value in polymeric systems. Since PDNBM has a tendency to form charge transfer complex (CT complex), a complexation behavior of PDNBM was investigated by using triethylamine as a donor. The UV spectra of the CT complexes of triethylamine with EtDNB and PDNBM are compared in Figure 4. Little difference was observed between the λ_{max} value (565 nm) of CT complexe absorptions in EtDNB and PDNBM. However, the absorption peak in the PDNBM complex became broader than that in the EtDNB complex. This phenomenon implies that the higher order complexes were formed in the polymer solution.

In addition to an increase in the λ_{max} value, a change in the concentration of CT complexes was observed. This is usually determined by a Benesi–Hildebrand analysis. As shown in Figure 5, the association constant K and the molar absorptivity ϵ of the CT complex were determined to be 8.8 L/mol and 4.5×10^3 mol⁻¹ cm⁻¹ for PDNBM, respectively. These values were larger than those (0.91 L/mol and 4.5×10^3 mol⁻¹ cm⁻¹) for EtDNB because in the polymer system, the CT complex might be stabilized by an interaction with its surrounding uncomplexed DNB chromophores.

Carrier Photogeneration in Polymer Blend Forming Charge Transfer Complex. Although for polymers containing the DNB group, photoconductivities such as photocurrent have been investigated,[3] detailed photoconductive behaviors such as carrier generation efficiency have not been studied. Recently, charge transfer complex of PDNBM using carbazole containing polymers as donor was reported.[4]

For films composed of an electron-donating polymer, poly(2-*N*-carbazolylethyl acrylate) (PCEA) and an electron-accepting polymer (PDNBM), photogeneration was examined. Since the film containing excess acceptor showed no photoresponse by the photodischarge technique, the film containing equal weights of a donor (donor:acceptor, 1.2:1 in molar ratio) and acceptor, which indicated the highest carrier generation efficiency, was used. This suggests that almost all generated carriers were composed

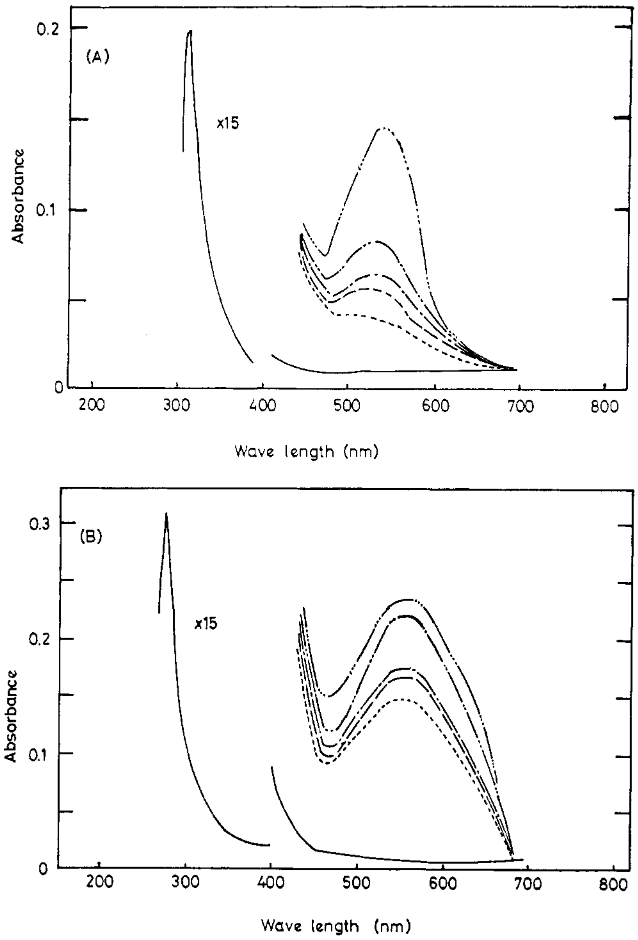

Figure 4. UV absorption spectrum of the charge transfer complexes. Ethyl 3,5-dinitrobenzoate (A) and poly[2-((3,5-dinitrobenzoyl)oxy)ethyl methacrylate] (B) with triethylamine. Total acceptor concentration 4.2 × 10^{-5} mol/L. Total donor concentration: 0 mol/L (—), 0.14 mol/L (- - -), 0.28 mol/L (— —), 0.42 mol/L (—·—), 0.56 mol/L (—··—), 0.70 mol/L (-····-).

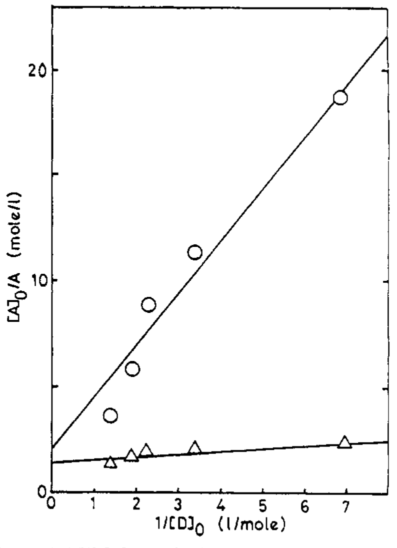

Figure 5. Benesi–Hildebrand plots for ethyl 3,5-dinitrobenzoate (△) and poly[2-((3,5-dinitrobenzoyl)oxy)ethyl methacrylate] (○) with triethylamine (20 °C, 565 nm, THF solution, 1-cm cell): A = absorbance, $[A]_0$ = total acceptor concentration, and $[D]_0$ = total donor concentration.

of holes and the generated electrons were captured by protonated nitro groups in the polymer blend.

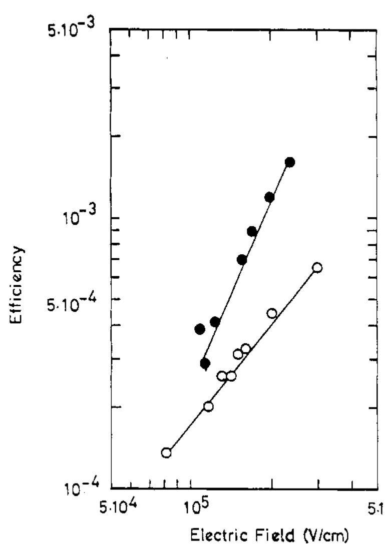

Figure 6. Carrier generation efficiency of sensitized poly[2-((3,5-dinitrobenzoyl)oxy)ethyl methacrylate] at 20 °C. Donor–acceptor ratio is D/A = 1.2:1. Doped with N-ethylcarbazole (●) and blend with poly(2-N-carbazolylethyl acrylate) (○).

For the PCEA–PDNBM polymer blend and N-ethylcarbazole (EtCz) in PDNBM, the field dependence of the carrier generation efficiency was compared in Figure 6. The efficiency strongly depended on the applied field. The carrier generation efficiency in this system was determined to be approximately 3.2 × 10^{-4} at 1.6 × 10^5 V/cm. This value was less than that (ca. 1 × 10^{-3} at 1.6 × 10^5 V/cm) in the 1:1 poly(N-vinylcarbazole)–TNF system.[11]

According to Onsager's theory,[12] the carrier generation has two processes. In the first step, the absorbed photon excites the electron from its ground state to an excited bound state. From the excited bound state, the electron may undergo thermalization and/or autoionization into a continuum state or may decay back to the ground state by emission of fluorescence, by a nonradiative process, or by combination with a hole. From this theory, the overall carrier generation efficiency may be given by

$$\phi(E) = \phi_0 \int f(r,\theta,E) g(r,\theta)\, \mathrm{d}^3 r$$

where ϕ_0 is the yield of electrons into the continuum states per absorbed photon, $f(r,\theta,E)$ is the probability of the dissociation of ion pairs, and $g(r,\theta)$ is the distribution of electrons from cationic center. It is reasonable to assume that the initial distribution of thermalized pairs is an isotropic δ function, so that r is equal to r_0 which is a characteristic thermalization length.

We calculated the parameters ϕ_0 and r_0 by using of the method which was reported by Pai et al.[13] The ϕ_0 value of ca. 0.1 for PCEA–PDNBM system was lower than that of ca. 0.15 for EtCz–PDNBM system, while the r$_0$ value of ca. 24 Å for the former system was higher than that of ca. 19 Å for the latter system. One possible reason for this result was that the interaction between donor and acceptor in PDEA–PDNBM system might be higher than that in EtCz–PDNBM system due to "polymer effect" and r_0 became higher. However, the polymer blend might not be perfectly miscible, and the irradiated light must have been scattered between separated phases. Very little of CT complex in the polymer blend was excited by the light irradiation and so ϕ_0 became lower.

As summary, PDNBM containing DNB group was a weak polymeric acceptor and indicated electron transport property. The low electron affinity lead to the relatively high electron drift mobility of PDNBM. However, the carrier generation efficiency of the donor-sensitized PDNBM was considerably low because of the low affinity as compared with PVK–TNF system.[13] The efficiency of the polymer blend containing PCEA was lower than EtCz–PDNBM. By the calculation according to Onsager's theory, it was found that the number of excited ion pairs was lower and the probability of the dissociation of ion pairs was higher for the polymer blend than those for EtCz–PDNBM system.

Registry No. PCEA·PDNBM, 118631-47-3; PDNBM, 82008-07-9; PDNBM·NEt_3, 118631-48-4; EtDNB·NEt_3, 118631-46-2; PDNBM·*N*-ethylcarbazole, 118631-49-5.

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Agarose Gel Electrophoresis of High Molecular Weight, Synthetic Polyelectrolytes

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ABSTRACT: The electric-field-induced motion of poly(styrenesulfonate) in agarose gels has been studied with two objectives, to probe the field-biased dynamics of polyelectrolyte chains in a porous matrix and to assess the quality of the molecular size fractionations that evolve as a result of these dynamics. For molecular weights from 7×10^3 to 15×10^6 the electrophoretic mobility of poly(styrenesulfonate) has been measured as a function of gel concentration, electric field strength, and ionic strength. High-resolution separations based on chain length have been observed for nearly all conditions, with the useful analytical range extending beyond the highest molecular weight examined. Mobilities qualitatively follow the experimental trends observed with DNA except in the ionic-strength dependence; a mobility maximum has been observed at intermediate ionic strengths for poly(styrenesulfonate) of low molecular weight, while a chain-length-independent mobility has been found at higher molecular weight when the ionic strength is low.

Introduction

Despite experimental simplicity and high resolution, gel electrophoresis has generally been neglected as a tool for measuring the molecular weight distributions of synthetic polymers. In sharp contrast, electrophoretic methods have become so ubiquitous in biopolymer research that complex protein and DNA mixtures are analyzed routinely.[1] We have been motivated by the success of such biopolymer applications to examine electrophoresis of highly charged, synthetic polymers. In this initial contribution attention will focus on electrophoretic migration of poly(styrenesulfonate) (PSS) in horizontal agarose gels. Synthetic polymers are heterogeneous in both chemical structure and size; how this heterogeneity affects electrophoretic behavior constitutes the biggest uncertainty in use of electrophoresis for characterizing synthetic polymer materials.

Chen and Morawetz[2] recently described electrophoresis of synthetic polymers in chemically cross-linked polyacrylamide gels, media conventionally employed to study proteins and small DNA fragments. For DNA chains less than 300 base pairs in length, polyacrylamide gel electrophoresis permits complete separation of mixtures when chain lengths differ by as little as one base pair. Chen and Morawetz limited their attention to PSS and poly(acrylic acid) samples with molecular weights in the range 2×10^4–1×10^5; we are primarily interested in molecular weights above this range. Separation in polyacrylamide gels will not be discussed further as the migration of a free polymer within these dense gels is likely to be somewhat different than in agarose gels.

Agarose gels are normally used for separations of molecules too large to penetrate the tighter pore structure of polyacrylamide gels. The largest proteins and higher molecular weight DNA chains fall in this category. Agarose gels are formed by physical cross-linking upon solution cooling, and the interconnecting strands are fiberlike molecular aggregates rather than individual chains.[3] The mean pore size depends on the concentration of agarose, with 100 nm being a characteristic length for a 1% gel.[3,4] Agarose is a polysaccharide possessing only a residual density of covalently bound ionizable groups.

Although size exclusion chromatography (SEC) is a valuable analytical tool for low and medium molecular weight polyelectrolytes, fractions of ultrahigh molecular weight ($M > 1.0 \times 10^6$) have generally resisted molecular weight analysis by SEC.[5,6] For this reason, synthetic polymers in this high molecular weight category have often been insufficiently characterized. Agarose gel electrophoresis could offer considerable advantages over difficult methods such as band sedimentation, which have been the only alternatives when SEC fails. The advantages of gel electrophoresis would include reduced cost, shorter run times, and increased ability to separate similarly sized fractions.

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