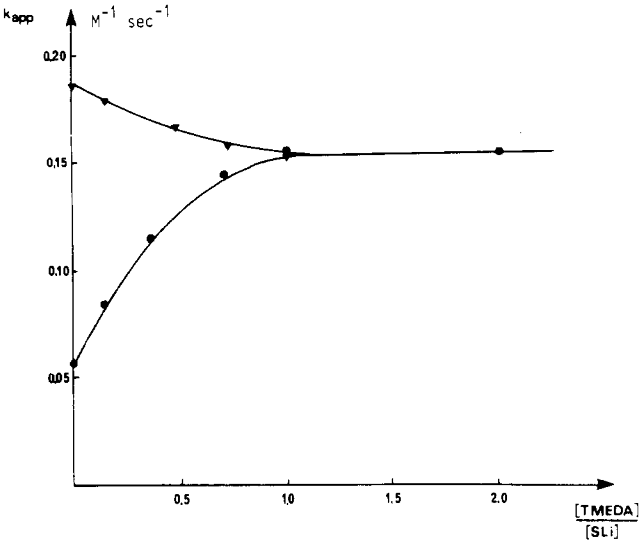

Figure 1. Effect of tetramethylethylene diamine on the apparent rate constant of propagation of polystyryllithium in cyclohexane: (▼) $[S^-,Li^+] = 9.2 \times 10^{-4}$ M; (●) $[S^-,Li^+] = 8.3 \times 10^{-3}$ M.

ment by assuming that at a reasonable value of $X = 1$ mM the addition of the complexing agent does not affect the rate of polymerization. Thus

$$k_p(K_{diss}/2)^{1/2} = 9.4 \times 10^{-3}\ M^{-1/2}\ s^{-1} \quad \text{at} \quad 25\ °C$$

compared with the reported, and directly determined, values of 5.3×10^{-3} $M^{-1/2}$ s^{-1} (ref 1) or 7.5×10^{-3} $M^{-1/2}$ s^{-1} (extrapolated from ref 3).

The above discrepancy may reflect experimental uncertainties or it may indicate a more complex structure of the studied system. Indeed we may consider a system in which the complexing agent is associated with the aggregated P^*_2 as well with the unaggregated P^*, i.e.,

$$P^* + C \rightleftarrows (P^*,C) \qquad K_{c^1}$$

$$P^*_2 + C \rightleftarrows (P^*_2,C) \qquad K_{c^2}$$

and assume that P^* and (P^*,C), but not P^*_2 or (P^*_2,C), are propagating. The balance equation aquires now the form

$$2[P^*]^2/K_{diss} + 2K_{c^2}[C][P^*]^2/K_{diss} + [P^*] + K_{c^1}[C][P^*] = X$$

Proceeding like previously we find

$$d[P^*]/d[C] = -(K_{c^1}[P^*] + 2K_{c^2}[P^*]^2/K_{diss})/(1 + 4[P^*]/K_{diss} + K_{c^1}[C] + 4K_{c^2}[C][P^*]/K_{diss})$$

and

$$dR/d[C] = k_cK_{c^1}[P^*] - (k_p + k_cK_{c^1}[C])(K_{c^1}[P^*] + 2K_{c^2}[P^*]^2/K_{diss})/(1 + 4[P^*]/K_{diss} + 4K_{c^2}[C][P^*]/K_{diss} + K_{c^1}[C])$$

For [C] = 0 the respective $dR/d[C]_{[C]=0}$ is given by

$$K_{c^1}[P^*] \times [k_c - k_p(1 + 2K_{c^2}[P^*]/K_{c^1}K_{diss})/(1 + 4[P^*]/K_{diss})]$$

Applying again the approximation $[P^*] \sim (K_{diss}/2)^{1/2}X^{1/2}$ and keeping in mind that $(4/2^{1/2})X^{1/2}/K_{diss}{}^{1/2} \gg 1$, we find that the plot of R versus [C] initially turns down when

$$X < (k_p/k_c)^2K_{diss}/8[1 - \tfrac{1}{2}(k_p/k_c)(K_{c^2}/K_{c^1})]^2$$

provided that $k_c < k_p$. This result, as expected, is identical with the previous one for $K_{c^2} = 0$. It leads on the whole to higher values of X for $K_{c^2} > 0$, but it demonstrates that K_{c^2}/K_{c^1} has to be smaller than $2k_p/k_c$. Provided that for $X = 1$ mM the addition of the complexing agent does not affect the rate of polymerization and taking the values of $k_c = 0.15$ M^{-1} s^{-1} and $k_p(K_{diss}/2)^{1/2} = 5.3 \times 10^{-3}$ $M^{-1/2}$ s^{-1} one finds

$$(k_p/k_c)(K_{c^2}/K_{c^1}) = 0.86$$

Since k_p/k_c is at least 500, one concludes that K_{c^2}/K_{c^1} is at the most 1.7×10^{-3}; i.e., the association of tetramethylethylenediamine with the dimer is expected to be considerably weaker than with the unaggregated polymer.

Consideration of still more complex systems is not warranted at this stage. Extention of these considerations to lithium polydienes may be interesting.

A Remark. C denotes the free complexing agent. The concentration of the added complexing agent, $[C_0]$, is given by $[C](1 + K_c[P^*])$ for the simple approach or by $[C](1 + K_{c^1}[P^*] + K_{c^2}[P^*_2])$ for the more elaborate one. However, $(dR/d[C_0])_{[C_0]=0} = 0$ only when $(dR/d[C])_{[C]=0}$ is also 0.

Registry No. SLi, 36345-04-7; $(H_3C)_2N(CH_2)_2N(CH_3)_2$, 110-18-9.

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Communications to the Editor

^{15}N Solid-State NMR Characterization of Aramid-Containing Nylon-6 by in Situ Polymerization with Benzoyl Caprolactam Derivatives

Polyamides and aramids are two important structural materials noted for their toughness, high modulus, and tensile strength.[1] They are currently used in a wide variety of applications as structural plastics and as reinforcing fibers in high-performance composites.

Natural abundance ^{15}N NMR spectroscopy has been used to characterize polyamides in solution.[2-5] ^{15}N NMR spectroscopy has several advantages over ^{13}C NMR including larger spectral width and simpler spectra. Characterization of polyamides by solution ^{15}N NMR is, however, hampered by the limited solubility of many polyamides, especially homo- and copolymers containing aromatic moieties. Polyamide nitrogens are subject to large chemical shift changes in the solvents needed to dissolve them.[6,7] Moreover, solution studies cannot duplicate the crystalline structure or hydrogen bonding in solid polyamides.

Recently, polyamic acid precursors to polyimides have been characterized by solid state ^{15}N CP-MAS NMR.[8] We had previously prepared and characterized several aliphatic/aromatic copolyamides based on caprolactam and several *N*-benzoyl caprolactam initiators (Figure 1).[9] In

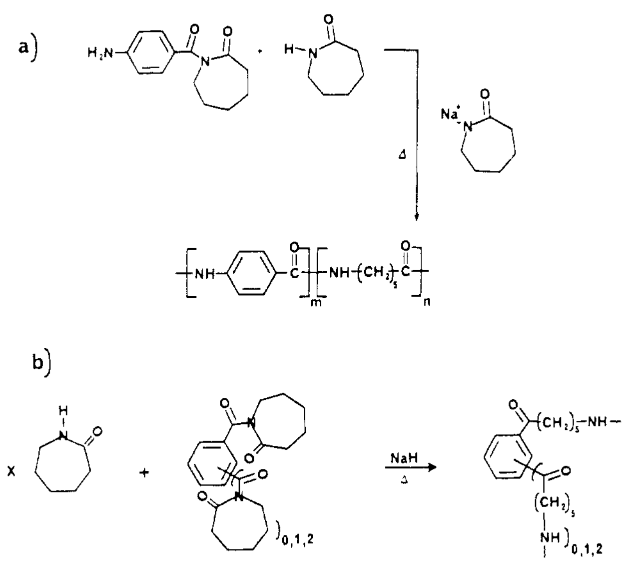

Figure 1. (a) Synthesis of aliphatic/aromatic block and alternating copolymers. (b) Synthesis of nylon-6 star polymers using trifunctional initiators.

Table I

	CP-MAS, ppm	solution, ppm
N-methylbenzamide	68.9	115.9
acetanilide	100.3	121.2
poly(*p*-benzamide)	95.7	
alternating copolymer	101.6, 80.9	118.1, 113.0
nylon-6 (annealed)	83.7	113.8
3-arm star nylon-6	87.3	113.8
nylon-6 (quenched)	84.1, 89.1	113.8

this paper we present the ^{15}N CP-MAS NMR results for several copolyamides along with model amides used for chemical shift assignments.

Experimental Section. Caprolactam homo- and copolymers were prepared as previously described.[9,10] Model amides were purchased from Aldrich Chemical Co. and used as received. ^{15}N solid-state CP-MAS measurements were made on a Bruker MSL-200 NMR spectrometer equipped with a Bruker MAS solids accessory. Measurements were made in a 4.7-T field corresponding to ^1H and ^{15}N frequencies of 200.13 and 20.287 MHz, respectively. Cross-polarization was performed using a 5-μs ^1H pulse and a contact pulse of 1–5 ms to meet the Hartmann–Hahn condition. MAS rotor speeds were 3.0–3.2 kHz. Sample temperature was maintained at 300 K. Spectral widths were 25 kHz. Between 20 000 and 50 000 scans were acquired for each sample with a delay of 3 s between scans. Chemical shifts are reported relative to glycine (δ = 0) as an external standard. Solution ^{15}N measurements were made by using an inverse-gated decoupling technique with a pulse width of 25 μs. All solution spectra were obtained in concentrated sulfuric acid solvent. $^{15}NH_4NO_3$ dissolved in D_2O was used as the reference (NH_4^+ = −353.5 ppm, glycine = −342.2 ppm) by inserting a tube containing the solution coaxially into the sample. Solution chemical shifts are referenced to the glycine scale used in the solid state (glycine = 0 ppm) and are reported as positive values.

Results and Discussion. ^{15}N chemical shifts of model amides and polyamides are listed in Table I. As expected the chemical shifts of the solid samples are approximately 30 ppm upfield of the solution resonances. Protonation of the amide carbonyl causes unpredictable shifts in ^{15}N resonances depending on the pK_a of the amide and solvent acidity.[6] Typical linewidths at half-height were 8–10 ppm. The solid-state chemical shifts of difunctional-initiated and star-initiated nylon-6 are similar to wholly linear nylon-6 although the star polymer is insoluble in concentrated H_2SO_4. We were disappointed to find that nitrogens on the initiator species were not visible in the spectrum. The low concentration of initiator (<1%) makes this technique inadequate without ^{15}N enrichment in the initiator. With atom enrichment, determination of the number of imide sites consumed would give the efficiency of initiation as well as confirm the synthesis of a star polymer.[10]

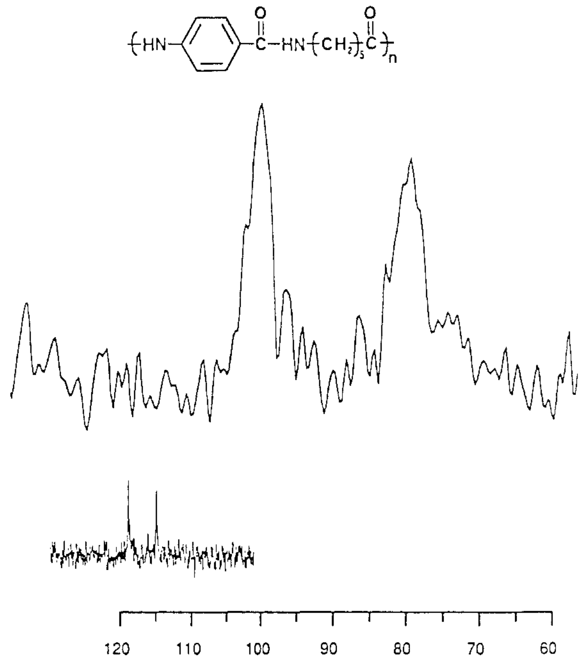

Figure 2. ^{15}N CP-MAS spectrum (upper trace) and ^{15}N solution spectrum (H_2SO_4) of poly(*p*-benzamide-*alt*-caproamide) alternating copolymer.

Figure 2 shows the ^{15}N CP-MAS spectra of a previously prepared copolymer of *p*-aminobenzoic acid and caprolactam with alternating aliphatic and aromatic units. This copolymer consists of only two types of amide nitrogens in equal proportions. The resonances at 101.6 and 80.9 ppm show equivalent areas consistent with the alternating copolymer structure. Comparison with the model acetanilide (100.6 ppm) indicates the downfield resonance is due to the aromatic substituent on the nitrogen. *N*-Methylbenzamide, however, lies well upfield of any other resonances in the table. It is apparently a poor model for an aliphatic-substituted amide in the copolymer. A possible explanation is that the methyl group of these models cannot duplicate the effects of an aliphatic chain on the nitrogen resonance. These "neighboring residue effects" have been recognized in solution ^{15}N experiments as well.[2-5] The solution ^{15}N spectrum of the copolymer in sulfuric acid is also shown and is consistent with the solid-state spectrum with the exception of large chemical shift changes.

Figure 3 shows a series of copolymers synthesized under conditions slightly different than those for the alternating copolymer. By altering conditions it was found that blocks of aromatic units could be generated in situ and incorporated into novel copolymers. Figure 3a shows a copolymer containing blocks of *p*-benzamide with few caprolactam units. The downfield shift of the ^{15}N resonance is consistent with nitrogen in a deshielding environment between an aromatic ring and carbonyl group. This shift also compared favorably with the ^{15}N spectrum of fully aromatic poly(*p*-benzamide) (95.7 ppm). Parts b and c of Figure 3 show copolymers containing 10% and 20%

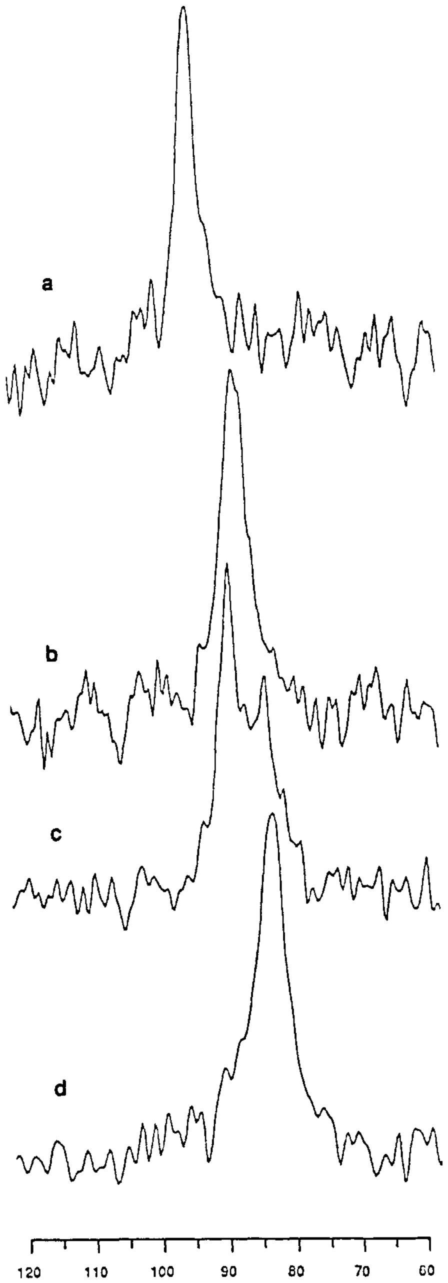

Figure 3. ^{15}N CP-MAS NMR spectra of block copolymers of caprolactam and *p*-aminobenzoic acid: (a) 80–90 mol % aromatic comonomer; (b) 10 mol % aromatic comonomer; (c) 20 mol % aromatic comonomer; (d) nylon-6 homopolymer.

aramid units, respectively, with the remainder being caprolactam units. The upfield shift is consistent with that of nylon-6 spectrum shown in Figure 3d. The copolymer peak, however, is 5–6 ppm downfield of the homopolymer. It is surprising that the presence of the aramid species causes such a shift even though the concentration is too low for the aramid ^{15}N resonances to be seen. Solution ^{15}N NMR of these samples gave a chemical shift identical with that of the nylon-6 homopolymer.

The presence of two crystal forms of nylon-6 is well-known and both have been previously characterized by IR and X-ray.[11,12] Parts a and c of Figure 4 show the ^{15}N NMR of γ and α crystal forms of nylon-6, respectively, while Figure 4b shows a mixture that is predominately α. Although ^{13}C and ^{15}N chemical shifts have been reported to be conformationally dependent,[13] the ^{13}C CP-MAS chemical shifts were identical for both crystal forms. It is clear that ^{15}N solid-state NMR is a better tool for differentiating the two crystal forms. Moreover, the chemical shifts correlate well with observed nylon-6 resonances seen in the copolymers in Figure 3. The ^{15}N solid-state NMR clearly shows that the nylon-6 blocks in the copolymers are mostly of the γ form.

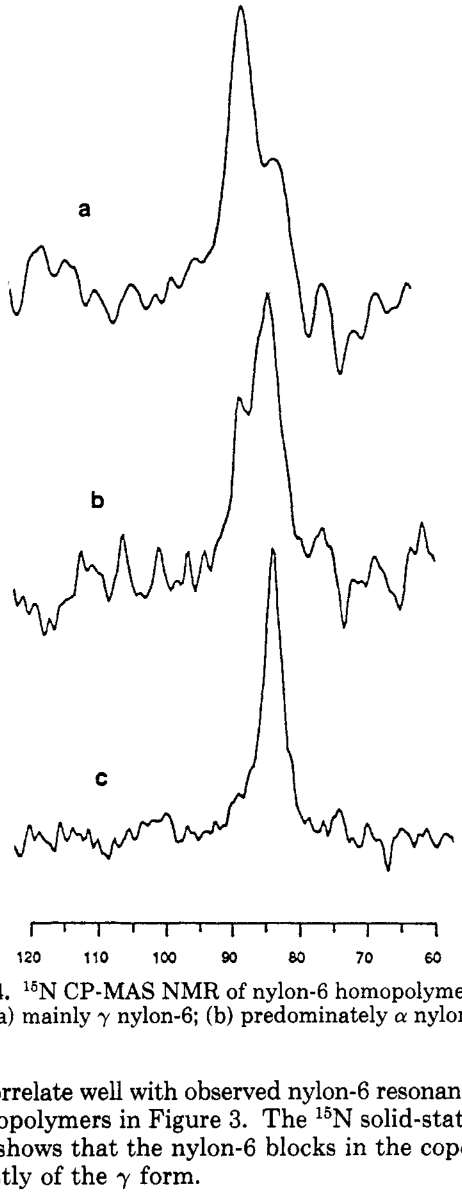

Figure 4. ^{15}N CP-MAS NMR of nylon-6 homopolymer crystal forms: (a) mainly γ nylon-6; (b) predominately α nylon-6; (c) α nylon-6.

Summary and Conclusion. Natural abundance ^{15}N NMR of solids has been demonstrated as a useful characterization tool for polyamides. In addition to copolymer composition differences, glassy amorphous conformations and crystal forms can be examined in the solid phase which are not observed in solution. ^{15}N CP-MAS NMR provides a new method for determining the crystal structures of nylon-6 samples. The greater sensitivity of nitrogen to its environment in solid-state NMR compared to carbon opens up a broad area for study of crystalline polyamides.

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Registry No. Nylon 6 (SRU), 25038-54-4; *N*-(*p*-aminobenzoyl)caprolactam (homopolymer), 102773-05-7; *N*-(*p*-aminobenzoyl)caprolactam (SRU), 53415-57-9; (*N*-(*p*-aminobenzoyl)-caprolactam)(ϵ-caprolactam) (block copolymer), 113811-13-5; *N*-methylbenzamide, 613-93-4; acetanilide, 103-84-4; poly(*p*-benzamide) (homopolymer), 25136-77-0; poly(*p*-benzamide) (SRU), 24991-08-0.

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Electron-Donor-Acceptor Copolyacrylates with High Photosensitivity

Since the success of the PVK-TNF complex in electrophotographic applications,[1] a number of studies have attempted to prepare copolymers containing intramolecular charge-transfer complexes.[2] Vinyl or acrylate/methacrylate compounds having a carbazole group were often employed as donor monomers, while acceptor monomers always contained strong electron-withdrawing units like nitro or cyano groups. In these investigations, due to either the high homopolymerizability of vinyl carbazole[3] or to inhibition of free radical copolymerization in particular by a nitrophenyl group,[4] it was extremely difficult to obtain copolymers with high enough molecular weights and good film quality. Hence, only a limited number of reports are available that describe the photoconductive properties of copolymers with intramolecular charge-transfer complexes.[5]

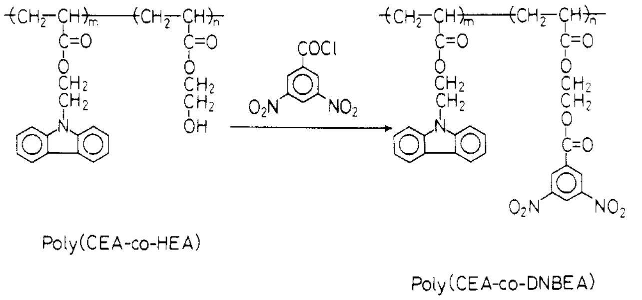
Previously we synthesized copolyacrylates having carbazole donor and trinitrofluorenone acceptor chromophores and first reported that the photogeneration efficiency of this electron-donor-acceptor (EDA) copolymer was higher than that of the donor polymer doped with the corresponding small acceptor molecule.[6] A similar effect was also confirmed for copolymers having a carbazole-containing acrylate and a dinitrobenzoate (DNB) containing methacrylate.[7] However, because of the low molecular weight resulting from inhibition of polymerization by acceptor monomers and high T_g's resulting from a specific interchain EDA interaction,[6-8] only samples with a low acceptor content (5 mol %) had the film quality required for the photogeneration measurement.

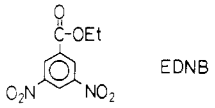
Table I
Properties of Poly(CEA-*co*-DNBEA)

sample	Cz cont,[a] mol %	DNB cont,[a] mol %	$\bar{M}_w$[b] × 10^4	$\bar{M}_n$[b] × 10^4	T_g,[c] °C
1	98.5	1.5	3.5	1.6	100
2	90	10	4.2	2.7	102
3	87	13	3.6	1.8	106
4	75	25	5.2	3.0	107
5	66	34	5.1	2.2	109
6	55	44	5.5	3.1	108

[a] Determined by 270-MHz ^1H NMR spectra in solutions in chloroform (for no. 1–3) and elemental analysis (for no. 4–6). [b] Determined by GPC with polystyrene as standard. [c] Determined by DSC.

To circumvent this problem, we chose an alternative way to prepare poly[(2-*N*-carbazolylethyl acrylate)-*co*-2-[[(3,5-dinitrobenzoyl)oxy]ethyl acrylate]] [poly(CEA-*co*-DNBEA)], viz., the reaction between dinitrobenzoyl chloride and the precursor copolymer, poly[(2-*N*-carbazolylethyl acrylate)-*co*-(2-hydroxyethyl acrylate)] [poly(CEA-*co*-HEA)] with different molar ratios of carbazole/hydroxyl groups. By this method, we succeeded in obtaining EDA copolyacrylates with rather low T_g's and high molecular weights (Table I), which could not be obtained from the direct copolymerization of corresponding acrylate monomers.[6,7,9] This enabled us to perform photoconductivity measurements on EDA copolymers with high contents of the acceptor chromophore. These EDA copolymers show definitely higher photosensitivities than the donor homopolymer doped with small acceptor molecules.





A typical synthetic procedure is as follows: To a solution of poly(CEA-*co*-HEA)[10] (200 mg, carbazole/hydroxyl ratio, 3/1) and dry pyridine (259 mg, 3.27 mmol) in 20 mL of dry THF, a solution of 3,5-dinitrobenzoyl chloride (754 mg, 3.27 mmol, 15-fold equiv to the hydroxyl group in the precursor copolymer) in 10 mL of anhydrous THF was added dropwise in 10 min with stirring. The stirring was continued for 48 h at 50 °C. After pyridinium hydrochloride was removed by filtration, the resulting polymer solution was poured into methanol, and the precipitates formed were reprecipitated thrice from THF into methanol, giving a bright yellow powder of the EDA copolymer. The reaction between poly(CEA-*co*-HEA) and dinitrobenzoyl chloride was quantitative since the IR absorption of the hydroxyl group around 3500 cm^{-1} disappeared from the resulting poly(CEA-*co*-DNBEA).

Films were prepared by pouring a THF solution of the copolymer onto NESA glass plates and drying in vacuo for at least 1 day. The thickness and surface area of films were 7 μm and 4 cm^2, respectively. Photosensitivity of copolymer films was determined by the photoinduced discharge technique used in the previous paper.[6,7,11] After corona charging to a positive surface potential, a film was exposed to monochromatic light from a 500-W xenon lamp through a grating monochromator. A photoinduced surface-potential decay was observed with a Monroe Model 263 isoelectric voltmeter through a transparent probe,

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