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(7) When hydrogen is replaced by fluorine in conjugated systems, steric effects are even more dramatic. A recent large-scale ab initio study [Dixon, D. A. *J. Phys. Chem.* **1986,** *90,* 2038] has shown that even in perfluoro-1,3-butadiene, where the chain is so short that 1,4 fluorine–fluorine repulsions are not present, 1,3 repulsions are sufficient to cause a nonplanar skew-*s*-*cis* conformation to be energetically favored.

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Dye Labeling Technique for Monitoring the Cure of Polyimides and Polyureas: Model Compound Studies

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Characterization of cross-linked polymers remains one of the challenging problems in polymer science. Our laboratory has been involved in developing new methods to probe cure reactions in network polymers. The approach we have taken is based on labeling by reactive dyes to mimic the curing agent and to use their photochemical and photophysical behavior to provide information on the curing process.

For example, we used a reactive label, *p,p*′-diaminoazobenzene (DAA) to monitor cure in epoxy–diamine resins. As the cure proceeds, $\lambda_{\max}$ of the $\pi \rightarrow \pi^*$ transition corresponding to the azo bond of DAA shows red-shifts (about 60 nm) in the visible spectra in a way that provides spectral discrimination for the cure products.[1] Furthermore, the fluorescence intensity of the DAA label at 560 nm increases sharply (more than 100 times), because of the fluorescence quantum yield of DAA increases more than a thousandfold when the amine groups of DAA become tertiary amines.[2] By analyzing visible and fluorescence spectra, we are able to obtain parameters characteristic of cure kinetics and mechanisms such as cure product composition, the reactivity ratio of primary and secondary amine, initial rate constants, and an activation energy of amine–epoxy reaction.[3,4] Finally, we compared experimental results with the theoretical predictions of Macosco and Miller on the weight average molecular weight and the soluble fractions.[4] In another epoxy–diamine system, we used *p,p*′-diaminostilbene as the reactive label, which showed red-shifts of only about 20 nm in the UV region.[5] Their fluorescence behavior was useful in correlating to the cure extent.

There is a tremendous interest in polyimides as high-temperature materials[6] and polyureas as new engineering materials.[7] In polyimides, the reaction of dianhydride with diamine first leads to the formation of amic acids followed by imidization. Cross-linking is often provided by acetylenic or norbonyl monomers. In polyureas, diisocyanate reacts with diamine to form ureas, whose secondary hydrogen can react further with isocyanate groups to form biuret-type cross-links.

In order to monitor the reaction products of these two polymers at various stages, we use a reactive label such as DAA to mimic the diamine component present in polyimide or polyurea synthesis. As the cure proceeds, the label shows spectral shifts in the UV–vis region corresponding to the various stages of the reaction. These shifts occur because of the distinctly different electronic states associated with each of the reaction products. Model compounds representing the various cure products have been synthesized and are shown in Scheme I.

Experimental Section

Solvents and Reagents. DAA was purchased from Eastman Kodak and recrystallized from methanol. Phthalic anhydride, dibutyltin dilaurate, and phenyl isocyanate were all purchased from Aldrich and used without further purification. *N*-methylpyrrolidone was purchased from Aldrich, distilled at reduced pressures, and stored over molecular sieve 4A. All other solvents were purchased from Aldrich and used without further purification.

Apparatus. Infrared spectra were recorded on a Nicolet 60SX FTIR spectrophotometer. UV–vis spectra were recorded on a Perkin-Elmer Lambda Array 3840 UV/vis spectrophotometer using NMP or Me_2SO as a solvent. Thermal analyses were carried out on a Omnitherm thermal analyzer with a DSC/DTA cell.

Synthesis. Model Diamic Acid. Diaminoazobenzene (0.50 g, 2.36 mmol) and phthalic anhydride (1.051 g, 7.08 mmol) were dissolved in 9 mL of glacial acetic acid, and the solution was stirred at room temperature for 1 h. The solution was poured into 25 mL of distilled water, and the yellow precipitate was collected by filtration. Recrystallization from ethanol yielded 0.887 g (74%) of diamic acid, mp 210–212 °C. The infrared spectra (KBr) showed absorptions at 3100 (νOH), 1665 (νC=O), 3278 (νNH), 1595 (νC=O), and 1541 cm^{-1} (νNH).

Model Amic Acid Imide. Aminonitroazobenzene (2.00 g, 8.27 mmol) and phthalic anhydride (1.94 g, 12.4 mmol) were refluxed in 50 mL of glacial acetic acid for 2 h, and the resulting precipitate was collected by filtration. The yellow solid was added to 40 mL of *N*-methylpyrrolidone and heated to reflux for 1 h. As the mixture cooled, fine crystals formed. These were collected and recrystallized from NMP to yield 1.99 g (64%) of imidonitroazobenzene (I).

The nitro group was reduced to an amine by refluxing I (0.60 g, 1.61 mmol) with $Na_2S \cdot 9H_2O$(6.58 g, 27.4 mmol) in 25 mL of 80% methanol for 1 h. The methanol was removed under vacuum, and the yellow precipitate was collected by filtration and rinsed with small portions of cold water. The solid was recrystallized from water to yield 0.30 g (54%) of aminoimidoazobenzene (II).

Phthalic anhydride (0.130 g, 0.878 mmol) and II (0.200 g, 0.585 mmol) were dissolved in 5 mL of NMP and heated to about 50 °C for 4 h. The solution was cooled and upon addition of water a red precipitate formed. Recrystallization from methanol yielded 0.136 g (51%) of amic acid imide: m.p. 240–242 °C. The infrared spectra (KBr) showed absorptions at 3100 (νOH), 1665 (νC=O) 3278 (νNH), 1595 (νC=O), 1541 (νNH), and 1720 and 1770 cm^{-1} (νNC=O).

Model Diimide. Imidization was accomplished by dissolving the pure diamic acid (0.50 g, 0.98 mmol) in 20 mL of DMF and refluxing for 2 h. The golden brown precipitate was collected by filtration and recrystallized in DMF to yield 0.37 g (80%) of diimide: mp 360–362 °C. The infrared spectra (KBr) showed no amide absorption but imide absorption at 1720 and 1770 cm^{-1}.

Model Diurea. DAA (0.53 g, 2.50 mmol) and phenyl isocyanate (3.25 mL, 29.7 mmol) were dissolved in chlorobenzene and heated to 120 °C for 2 h under N_2 purge. The yellow precipitate was collected by filtration and recrystallized from Me_2SO/acetone to yield the diurea. The infrared spectra (KBr) showed absorptions at 3280 (νNH), 1635 (νC=O), 1590 (νNH), and 1540 cm^{-1} (νCNH).

Model Dibiuret. The diurea of DAA (0.45 g, 1.0 mmol) was dissolved in 25 mL of Me_2SO with dibutyltin dilaurate catalyst (25 mg, 0.04 mmol) and phenyl isocyanate (3.25 mL, 29.7 mmol). The solution was heated to 85 °C for 2 h and the excess phenyl isocyanate was removed under vacuum. Water was added, and the precipitated product was collected by filtration and dried. This crude compound was purified by column chromatography with an acetone/heptane mixture (4/5) to yield the dibiuret: mp 206 °C. The infrared spectra (KBr) showed absorptions at 3450 (νnH), 1635 (νC=O), 1590 (νNH), 1540 (νCNH), and 1690 cm^{-1} (ν biuret NC=O).

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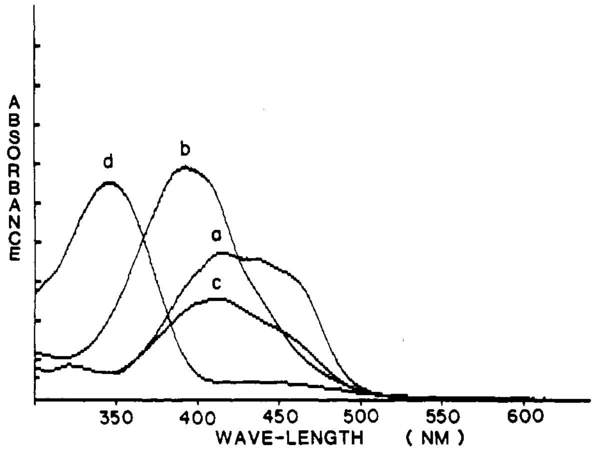


Figure 1. UV–visible spectra of DAA (a), diamic acid (b), imide amic acid (c), and diimide (d) in *N*-methylpyrrolidone.

Table I
Absorption Maxima, Spectral Shifts, and Extinction Coefficients of Model Compounds

solvent	compd	λ_{max}, nm	$\Delta\lambda$,[a] nm	ext coeff $\times 10^{-4}$,[b] L/(mol·cm)
1.3×10^{-5} M NMP	DAA (a)	415	0	4.5
	diamic acid (b)	393	−22	3.9
	imide/amic acid (c)	413	+20	2.0
	diimide (d)	343	−68	3.0
2.5×10^{-5} M Me_2SO	DAA (a)	415	0	4.5
	diurea (e)	392	−23	3.8
	dibiuret (f)	328	−64	2.3

[a] This is the successive spectral shift. [b] Due to the possible impurities, these should be taken as approximate values.

Results and Discussion

Model Compounds for Polyimides. Model compounds representing the various cure products have been synthesized and their structures confirmed by infrared spectroscopy. Figure 1 demonstrates the successive shifts occurring in the UV–vis spectra as DAA reacts with phthalic anhydride to form the products shown in Scheme I. Figure 1a shows the main absorption peak at 415 nm due to the $\pi \rightarrow \pi^*$ transition of the azo bond in DAA. This electronic transition is blue-shifted to 393 nm in the diamic acid derivative (Figure 1b) because of the weaker electron-donating capacity of the amide as compared to the amine.[8] When imidization occurs on one side of the molecule, a red-shift of about 20 nm resuts from the greater resonance induced by the push–pull effect of the amide–imide combination (Figure 1c). Sawicki attributed these bathochromic shifts to the decreased energy of the zwitterionic resonance structures.[8]

Complete imidization destroys this effect and greatly reduces the electron density near the azo linkage. Thus, a large blue-shift is observed and the $\pi \rightarrow \pi^*$ transition is shifted to 343 nm, as shown in Figure 1d. This trend is consistent with the blue-shifts observed when 4-aminoazobenzene is converted to 4-imidoazobenzene in 95% ethanol.[8] These shifts along with the extinction coefficients of the model compounds have been summarized in Table I. The extinction coefficients are all in the same order of magnitude.[10] Due to the possible impurities, these values should be taken as approximate values. Sawicki[8] reports similar extinction coefficients for 4-amino-, 4-amido-, or 4-imidoazobenzenes. In order to test the experimental results, semiempirical calculations of the spectral shifts and the extinction coefficients using the INDO/S-CI method[9] are currently under way in our laboratory. Recently, Ushiki et al.[10] reported the absorption spectra of azoaromatic polyimides based on DAA when dissolved in 97% sulfuric acid. However, since their azo groups are in the protonated forms, which are known to cause large red-shifts,[11] our absorption maxima cannot be compared with theirs. In fact, our diimide model compound shows a maximum at 457 nm in 97% sulfuric acid, in comparison to 353 nm in *N*-methylpyrrolidone.

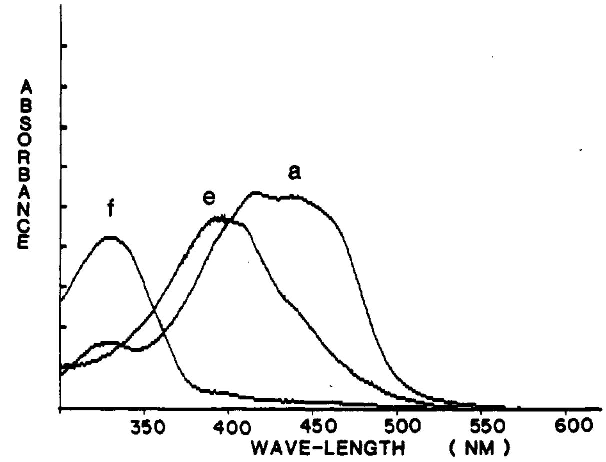


Figure 2. UV–visible spectra of DAA (a), diurea (e), and dibiuret (f) in Me_2SO.

Labeled polyimides were also synthesized, and similar shifts were observed in both neat films and dilute solution. Polyimides made from monomers with fluorinated alkyl bridges are best suited for labeling with DAA because the matrix absorption occurs at a much lower wavelength than the label's absorption.

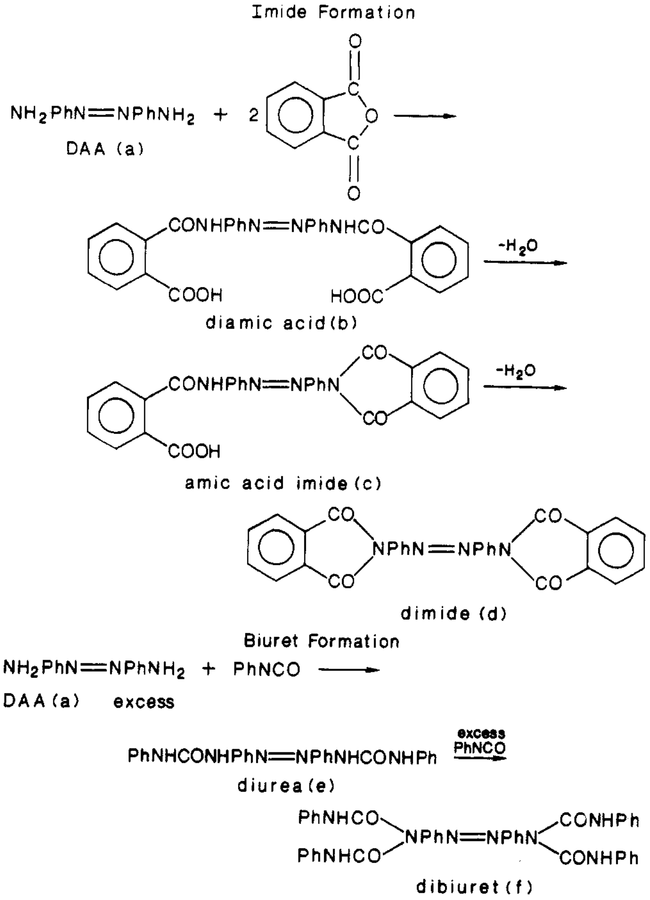
Model Compounds for Polyureas. Figure 2 demonstrates the successive shifts in the UV–vis spectra as the diamine DAA is reacted with excess phenyl isocyanate to form urea (e) and biuret (f) bonds, as shown in Scheme I. When diurea is reacted with excess phenyl isocyanate, NH groups attached to the phenyl ring will be converted to biurets. However, such biurets are not expected to have much influence on the absorption of the label. The shifts observed in Figure 2e,f are similar to those occurring during imidization because of the decreased electron-donating capacity of the urea group and the strong electron-withdrawing effect of the biuret group, as summarized in Table I.

Conclusion

The successive blue- and red-shifts as well as extinction changes in the coefficients are observed in the UV–vis absorption of the reactive label DAA as it is converted to biuret and imide compounds. These shifts are due to the unique electronic environment surrounding the azo bond for each of the reaction products. Especially important are the large blue-shifts accompanying complete imidization and biuret formation which enable us to distinguish, for example, diimide from amic acid imide. By taking advantage of this ability, we are investigating the kinetics of the imide ring formation known to proceed by fast and slow first-order processes.[12]

In cases where the matrix absorbs near the biuret or imide bands, digital subtraction with an increased dye label concentration will be required. Alternatively, a label with absorption maxima at longer wavelengths (e.g., ~500 nm)

Scheme I



could be used so that even after blue-shifts occur the matrix absorption will not interfere with the label's absorption.

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Registry No. I, 107302-25-0; **II**, 107302-26-1; **b**, 107302-27-2; **c**, 107302-28-3; **d**, 107302-29-4; **e**, 74261-74-8; **f**, 107302-30-7; **DAA**, 538-41-0; PhNCO, 103-71-9; 4,4-$H_2NC_6H_4N{=}NC_6H_4NO_2$, 730-40-5; phthalic anhydride, 85-44-9.

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Synthesis and Cationic Polymerization of 3,9-Dibenzyl-1,5,7,11-tetraoxaspiro[5.5]undecane

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Several spiro orthocarbonates, 1,5,7,11-tetraoxaspiro[5.5]undecane (**1**),[1] 3-methylene-1,5,7,11-tetraoxaspiro[5.5]undecane (**2**),[2] 3,9-dimethylene-1,5,7,11-tetraoxaspiro[5.5]undecane (**3**),[3] and 8,10,19,20-tetraoxaspiro[5.2.2.5.2.2]henicosane (**4**),[4] undergo ring-opening transfer polymerization in the presence of cationic catalysts to give alternating copolymer, poly(ether carbonate). Bailey and Endo have shown that the spiro orthocarbonate (SOC) is one of the useful monomers that undertake expansion in volume upon polymerization.[5] Boron trifluoride and tin(IV) chloride are known to initiate cationic polymerization of SOCs at varying temperature.[1-4] On the other hand, we have carried out the polymerization of **1** with some sulfonium salts as thermal latent cationic catalysts at 80–120 °C.[6] Since the SOC might be a promising monomer as, e.g., a resin additive with enhancement of adhesion on curing,[7] it is important to make clear reactivity of SOCs for their functionalization or materialization. However, the SOCs hitherto used are fairly sensitive to moisture, so that scrutiny of the reactivity toward cationic catalysts has not been done yet.

Recently, we have prepared a SOC, 3,9-dibenzyl-1,5,7,11-tetraoxaspiro[5.5]undecane (**5**), which is stable enough to moisture to study in detail. In this paper, synthesis of **5** and effectiveness of various cationic catalysts in the polymerization of **5** are described.

Experimental Section

Materials. Commercially available *p*-toluenesulfonic acid monohydrate was dehydrated by heating at 100 °C for 6 h in vacuo, giving brown solid which was directly used as a catalyst. Boron trifluoride etherate, titanium(IV) chloride, and *n*-butyl iodide were purified by distillation just before use. Benzyltetramethylenesulfonium hexafluoroantimonate was prepared according to the method reported previously by us.[8] As for cationic catlysts other than those stated above, each extra pure grade reagent was used as first use without purification.

Characterization. Molecular weight and its dispersion were measured by Toyo Soda HPLC CCP&8000 using TSK gel G2500H and G3000H (solvent, THF). IR spectra were recorded with JEOL FT/IR-3. NMR spectra were obtained by JEOL PMX-60 (60 MHz) and FX-100 (100 MHz).

Diethyl Benzylmalonate (6). To sodium ethoxide solution prepared from sodium (10.8 g, 0.47 mol) and 450 mL of absolute ethanol, diethyl malonate (150 g, 0.94 mol) and then benzyl chloride (59.3 g, 0.47 mol) were added dropwise at room temperature. The resulting mixture was refluxed for 2 h. After cooling, the reaction mixture was diluted with water and subsequently extracted with ether. The ether layer was dried over anhydrous magnesium sulfate and evaporated. The residue was purified by distillation to give 100 g (86%) of **6**, bp 129–130 °C/0.15 mmHg.

2-Benzyl-1,3-propanediol (7). To a suspension of $LiAlH_4$ (40.0 %, 1.1 mol) in absolute ether (1.3 L), the diester (**6** 100 g, 0.40 mol) was added dropwise at room temperature. After the addition, the mixture was refluxed for 4 h and stirred overnight at room temperature. A saturated sodium sulfate solution was slowly added into the reaction mixture. A white mass was filtered off, and the filtrate was evaporated. The residual white solid was recrystallized from benzene. Yield: 59.2 g (87%). Mp: 64–66 °C.

3,9-Dibenzyl-1,5,7,11-tetraoxaspiro[5.5]undecane (5). Preparation of **5** followed the previously reported method for **1**.[9] A mixture of **7** (25.0 g, 0.75 mol), tetraethyl orthocarbonate (**8**,