Preparation of New Polymers Containing an Azobenzene Group in the Side Chain by Palladium-Catalyzed Polymer Reaction and Polycondensation and Characterization of the Polymers

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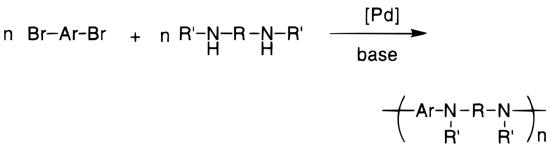
ABSTRACT: Palladium-catalyzed amination of poly(*p*-bromostyrene) with 4-(phenylamino)azobenzene afforded polystyrene derivative having an aminoazobenzene group in the side chain with a high degree of substitution. Palladium-catalyzed polycondensation of aryl dibromides with 4-aminoazobenzene also gave poly(iminoarylene)s having azobenzene group in the side chain in good yields. Photoinduced and thermal cis−trans isomerization behaviors of the polymers were investigated. Comparison of isomerization rate constants and activation energy values of the polymers and the corresponding model compound showed little difference in the kinetics data between the polymers, thus suggesting no significant influence of the structure of the polymer backbone on the azobenzene cis−trans isomerization. The absorption spectra of the polymers were dependent on the acidity of media because it can exist in neutral and protonated forms.

Introduction

Azobenzene is a well-known photosensitive chromophore, which undergoes photoinduced and thermal cis−trans isomerization. Owing to the photoactivities, a large number of polymers containing azobenzene group have attracted interest because of their potential uses in various photonic applications.[1]

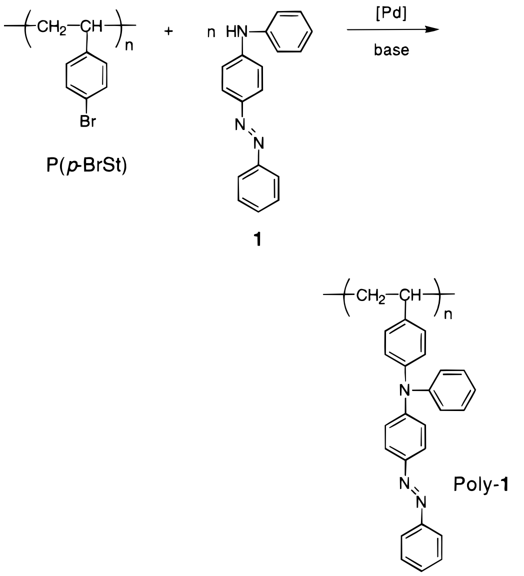
On the other hand, polymer syntheses using organotransition-metal complexes as catalysts are the subject of recent interest,[2] and various bond formation processes involving the reaction of two kinds of functional groups catalyzed by organometallic complexes have been applied to the polycondensation reactions of bifunctional organic compounds to give novel poly(arylene)s, aromatic polyesters, polyamides, and the related polymers.[2a,b,3] Recently, catalytic amination reactions of aryl halides with amines using palladium complexes have been investigated,[4] and preparation of poly(arylenediamine)s by the Pd-catalyzed polycondensation of aryl dibromides with diamines has also been reported.[5]



$$n\ \mathrm{Br{-}Ar{-}Br} + n\ \mathrm{R'{-}\underset{H}{N}{-}R{-}\underset{H}{N}{-}R'} \xrightarrow[\text{base}]{[\mathrm{Pd}]} \left(\mathrm{Ar{-}\underset{R'}{N}{-}R{-}\underset{R'}{N}}\right)_n \qquad (1)$$

Since the Pd-catalyzed amination reaction offers advantages over the classical methods, which require either activated substrates or severe reaction conditions, the Pd-catalyzed polycondensation could provide various regiodefined polyamines by changing the structure of the aryl dibromides and diamines. Furthermore, a solid-phase synthesis of arylamines via the Pd-catalyzed amination of resin-bound aromatic bromides with amines has also been reported.[6]

These observations prompted us to apply the Pd-catalyzed amination to preparation of polymers containing functional groups in the side chains. Thus, we have carried out the Pd-catalyzed polymer reaction of poly(*p*-bromostyrene) [P(*p*-BrSt)] with 4-(phenylamino)azobenzene (**1**) and the Pd-catalyzed polycondensation of 1,3-dibromobenzene with 4-aminoazobenzene (**2**).



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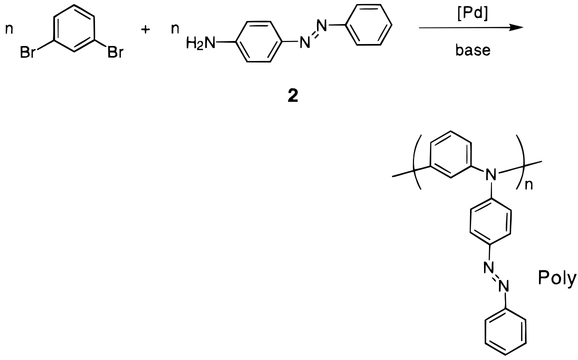

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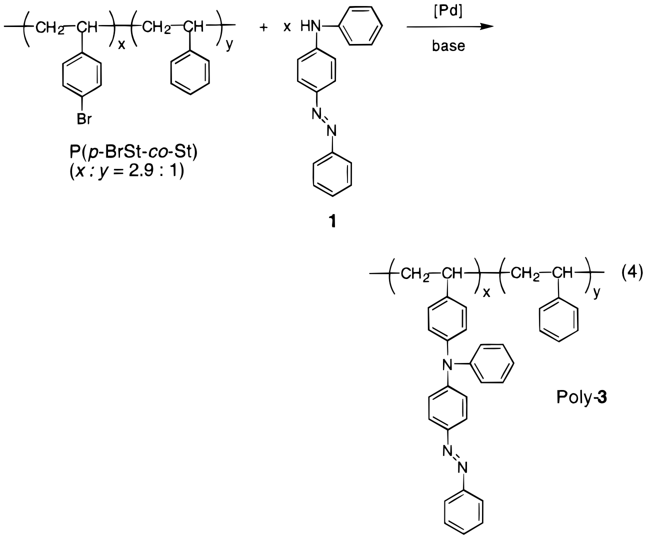
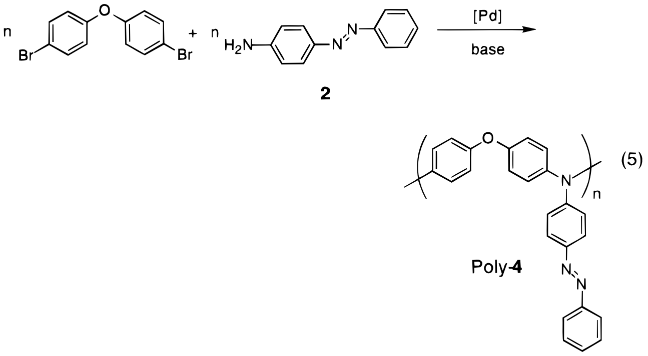
These polymers have an azobenzene structure in their side chains and are expected to show photochromic and thermochromic properties similar to those of the reported polymers containing azobenzene groups. We have also carried out the Pd-catalyzed polymer reaction of poly(*p*-bromostyrene-*co*-styrene) [P(*p*-BrSt-*co*-St)] with **1** and the Pd-catalyzed polycondensation of bis(4-bromophenyl) ether with **2**, and a comparison of their optical properties is also reported. Some of the results have been reported in a communication.[7]





Experimental Section

Materials. P(*p*-BrSt) was prepared by radical polymerization of *p*-bromostyrene in the presence of 2,2′-azobisisobutyronitrile (AIBN) in benzene at 60 °C under nitrogen.[8] Radical copolymerizations of styrene and *p*-bromostyrene were carried out analogously. **1**, **2**, and bis(4-bromophenyl) ether were purified by recrystallization from ethanol. Tris(dibenzylideneacetone)dipalladium(0) [$Pd_2(dba)_3$] was prepared by the reported method.[9] Toluene was distilled from CaH_2 and stored under N_2.

Polymer Reaction. A mixture of P(*p*-BrSt) (275 mg, 1.5 mmol of monomer unit) and **1** (1230 mg, 4.5 mmol) was dissolved in toluene (25 mL). Sodium *tert*-butoxide (NaO-*t*-Bu) (216 mg, 2.25 mmol), $Pd_2(dba)_3$ (34 mg, 0.0375 mmol), and tri-*tert*-butylphosphine [P(*t*-Bu)$_3$] (46 mg, 0.225 mmol) were added to the solution at room temperature. The reaction mixture was stirred at 100 °C for 24 h under N_2. After cooling to room temperature, the mixture was quenched by adding aqueous ammonia (100 mL) and the product was extracted with $CHCl_3$ (100 mL). The organic fraction was concentrated and reprecipitation from $CHCl_3$/methanol three times gave an orange powder of Poly-**1** (550 mg, relative recovery of polymer 99%). Anal. Found: C, 82.8; H, 5.7; N, 11.1; Br, 0.0. Calcd for $(C_{26}H_{21}N_3)_n$: C, 83.2; H, 5.6; N, 11.2. IR (KBr, cm^{-1}): 3040 (w), 2950 (w), 1590 (s), 1493 (s), 1313 (s), 1282 (s), 1140 (m), 833 (m), 767 (m), 690 (m). ^1H NMR (400 MHz in $CDCl_3$, ppm): $\delta = 1.2-2.2$ (3H), 6.4−7.2 (11H), 7.3 (3H), 7.6 (2H), 7.7 (2H). ^{13}C NMR (100 MHz in $CDCl_3$, ppm): $\delta = 40.2$, 121.5, 122.5, 124.3, 125.4, 128.9, 129.4, 130.1, 139−142, 144.7, 146.8, 150.2, 152.7.

Other polymer reactions were carried out similarly. Poly-**3** (x:y = 2.9:1): relative recovery of polymer 95%. Anal. Found: C, 83.6; H, 5.9; N, 10.2; Br, 0.0. Calcd for $[(C_{26}H_{21}N_3)_{2.9} + (C_8H_8)]_n$: C, 84.0; H, 5.8; N, 10.2. IR (KBr, cm^{-1}): 3025 (w), 2915 (w), 1590 (s), 1494 (s), 1313 (s), 1282 (s), 1140 (m), 833 (m), 766 (m), 689 (m). ^1H NMR (400 MHz in $CDCl_3$, ppm): $\delta = 1.1-2.4$, 6.4−6.9, 7.0, 7.4, 7.7. ^{13}C NMR (100 MHz in $CDCl_3$, ppm): $\delta = 40.2$, 121.4, 122.5, 124.2, 125.3, 128.9, 129.4, 130.1, 140.9, 144.6, 146.7, 150.3, 152.8.

Polycondensation. A mixture of 1,3-dibromobenzene (472 mg, 2 mmol) and **2** (394 mg, 2 mmol) was dissolved in toluene (15 mL). NaO-*t*-Bu (577 mg, 6 mmol), $Pd_2(dba)_3$ (46 mg, 0.05 mmol), and P(*t*-Bu)$_3$ (61 mg, 0.3 mmol) were added to the solution at room temperature. The reaction mixture was stirred at 100 °C for 24 h under N_2. After cooling to room temperature, the mixture was quenched by adding aqueous ammonia (50 mL) and the product was extracted with $CHCl_3$ (50 mL). The organic fraction was concentrated, and reprecipitation from $CHCl_3$/methanol and thoroughly washing with methanol and ether gave an orange powder of Poly-**2** (495 mg, 91% yield). Anal. Found: C, 78.7; H, 5.2; N, 14.5; Br, 0.0. Calcd for $(C_{18}H_{13}N_3)_n$: C, 79.7; H, 4.8; N, 15.5. IR (KBr, cm^{-1}): 3063 (w), 1585 (s), 1484 (s), 1297 (s), 1140 (m), 839 (m), 767 (m), 688 (m), 548 (m). ^1H NMR (400 MHz in $CDCl_3$, ppm): $\delta = 6.8$ (2H), 6.9−7.1 (4H), 7.3 (3H), 7.7 (4H). ^{13}C NMR (100 MHz in $CDCl_3$, ppm): $\delta = 120.5$, 121.4, 122.1, 122.6, 124.2, 128.9, 130.2, 130.4, 147.4, 147.5, 149.5, 152.6.

Other polycondensation reactions were carried out in an analogous way. Poly-**4**: 83% yield. Anal. Found: C, 79.2; H, 5.0; N, 10.7; Br, 0.0. Calcd for $(C_{24}H_{17}N_3O)_n$: C, 79.3; H, 4.7; N, 11.6. IR (KBr, cm^{-1}): 3038 (w), 1593 (s), 1492 (s), 1312(m), 1227 (s), 1140 (m), 831 (m), 766 (m), 688 (m). ^1H NMR (400 MHz in $CDCl_3$, ppm): $\delta = 7.0$ (4H), 7.1 (2H), 7.1 (4H), 7.3 (1H), 7.4 (2H), 7.7−7.9 (4H). ^{13}C NMR (100 MHz in $CDCl_3$, ppm): $\delta = 119.8$, 120.2, 122.4, 124.3, 127.0, 128.9, 130.1, 142.1, 146.7, 150.6, 152.8, 153.7.

Preparation of the Model Compound. A model compound of the polymers, 4-[phenyl(*p*-tolyl)amino]azobenzene (Model-**1**), was also prepared analogously by the Pd-catalyzed amination of 4-bromotoluene (257 mg, 1.5 mmol) with **1** (410 mg, 1.5 mmol). Purification of Model-**1** was carried out by column chromatography ($CHCl_3$/hexane = 1/1) (538 mg, 99% yield). Anal. Found: C, 82.5; H, 6.0; N, 11.5; Br, 0.0. Calcd for $C_{25}H_{21}N_3$: C, 82.6; H, 5.8; N, 11.6. IR (KBr, cm^{-1}): 3023 (w), 1590 (s), 1508 (s), 1493 (s), 1328 (s), 1281 (s), 1140 (m), 848 (m), 813 (m), 768 (m), 691 (m). ^1H NMR (400 MHz in $CDCl_3$, ppm): $\delta = 2.3$ (s, 3H), 6.9−7.1 (m, 9H), 7.2 (dd, 2H), 7.3 (t, 1H), 7.4 (dd, 2H), 7.7 (d, 2H), 7.8 (d, 2H). ^{13}C NMR (100 MHz in $CDCl_3$, ppm): $\delta = 20.9$, 120.9, 122.5, 123.9, 124.2, 125.2, 126.0, 129.0, 129.4, 130.1, 130.2, 134.2, 144.3, 146.9, 147.0, 150.8, 153.0.

Measurement. IR and NMR spectra were recorded on a JASCO FT/IR-230 spectrometer and a JEOL JNM-A400 NMR spectrometer, respectively. Elemental analyses were carried out with a Yanaco CHN Corder MT-5 and a Mitamura Riken Kogyo Micro Elementary Analyzer. GPC analyses were performed with a JASCO 880 system using a Shodex K-804L column ($CHCl_3$ as an eluent) or using a Tosoh TSK-Gel G4000 HHR column [a DMF solution of LiCl (0.01 M) as an eluent]. Calibration curves for GPC were made by use of polystyrene standards. UV−visible absorption spectra were recorded on a Shimadzu UV-1600 spectrometer. Photoirradiation was carried out with a high-intensity projecting lantern (WACOM HX-500 Q/P with a 500 W ultrahigh-pressure mercury lamp), and the wavelength was selected at about 405 nm using Corning 7-59 cutoff filter and an aqueous solution filter (0.25 M $NaNO_3$ + 0.1 M $NaNO_2$).[10] The photoinduced and thermal isomerization behaviors of the samples were observed by monitoring the

Table 1. Palladium-Catalyzed Modification of P(*p*-BrSt) and P(*p*-BrSt-*Co*-St) with 1[a]

run	polymer[b]	ligand[c]	DS[d]/%	recovery of polymer[e]/%	M_n[f] × 10^{-4}	M_w[f] × 10^{-4}
1	P(*p*-BrSt)	P(*t*-Bu)$_3$	96	99	3.1	4.0
2	P(*p*-BrSt)	P(*o*-tolyl)$_3$	54	87	2.7	3.6
3	P(*p*-BrSt)	BINAP	4	90	1.7	2.6
4	P(*p*-BrSt)	*p*-tolyl-BINAP	3	71	1.8	2.5
5	P(*p*-BrSt)	DPPP	5	78	1.7	2.2
6	P(*p*-BrSt)	none[g]	0	81	1.8	2.3
7	P(*p*-BrSt-*co*-St)	P(*t*-Bu)$_3$	98[h]	95	3.1	3.9

[a] Polymer reactions were carried out in the presence of NaO-*t*-Bu (1.5 equiv for the *p*-bromostyrene unit), Pd$_2$(dba)$_3$ (2.5 mol % for the *p*-bromostyrene unit), and ligand (P/Pd ratio = 3/1) in toluene at 100 °C for 24 h. [b] P(*p*-BrSt) = poly(*p*-bromostyrene) [$M_n = 1.9 \times 10^4$, $M_w = 2.5 \times 10^4$ (GPC)], P(*p*-BrSt-*co*-St) = poly(*p*-bromostyrene-*co*-styrene) [*p*-BrSt/St = 2.9/1; $M_n = 2.0 \times 10^4$, $M_w = 2.5 \times 10^4$ (GPC)]. [c] P(*t*-Bu)$_3$ = tri-*tert*-butylphosphine, P(*o*-tolyl)$_3$ = tri-*o*-tolylphosphine, BINAP = 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl, *p*-tolyl-BINAP = 2,2′-bis(di-*p*-tolylphosphino)-1,1′-binaphthyl, DPPP = 1,3-bis(diphenylphosphino)propane. [d] DS = degree of substitution; the values were calculated from C/N ratios. [e] The relative recoveries of the polymers were calculated on the basis of the charged amount of P(*p*-BrSt) or P(*p*-BrSt-*co*-St), taking into account the degree of substitution. [f] Calibrated by GPC (CHCl$_3$, polystyrene standards). [g] No catalyst was added. [h] The value was calculated on the basis of the charged amount of *p*-bromobenzene unit.

Table 2. Palladium-Catalyzed Polycondensation of Aryl Dibromides with 2[a]

run	aryl dibromide	ligand	yield[b]/ %	M_n[c] × 10^{-3}	M_w[c] x 10^{-3}
1	1,3-dibromobenzene	P(*t*-Bu)$_3$	91	7.0	9.0
2	1,3-dibromobenzene	P(*o*-tolyl)$_3$	14	2.0	2.6
3	1,3-dibromobenzene	BINAP	20	2.1	2.7
4	1,3-dibromobenzene	DPPF[d]	21	1.4	1.9
5	1,3-dibromobenzene	none[e]	0		
6[f]	1,3-dibromobenzene	P(*t*-Bu)$_3$	0		
7	bis(4-bromophenyl) ether	P(*t*-Bu)$_3$	83	7.1[g]	18.6[g]

[a] Reactions were carried out in the presence of NaO-*t*-Bu (3 equiv for monomer), Pd$_2$(dba)$_3$ (2.5 mol % for monomer), and ligand (P/Pd ratio = 3/1) in toluene at 100 °C for 24 h. [b] Insoluble fraction in methanol and ether. [c] Calibrated by GPC [LiCl/DMF (0.01 M), polystyrene standards]. [d] DPPF = 1,1′-bis(diphenylphosphino)-ferrocene. [e] No catalyst was added. [f] Reaction was run with Cs$_2$CO$_3$ (3 equiv for monomer) as base. [g] Calibrated by GPC (CHCl$_3$, polystyrene standards).

changes in the absorbance (at 430 nm) with time at constant temperatures with the UV−visible absorption spectrometer.

Results and Discussion

Preparation. Recent reports on the Pd-catalyzed aryl amination have demonstrated mechanisms of the reaction and improved catalyst systems.[4] Table 1 summarizes the results of the Pd-catalyzed modification of P(*p*-BrSt) or P(*p*-BrSt-*co*-St) with **1** using various catalyst systems. The degree of substitution (DS) was determined by elemental analysis. In the present study, use of a catalyst system generated from Pd$_2$(dba)$_3$ and P(*t*-Bu)$_3$ was found to give the highest DS value for the amination of P(*p*-BrSt) with **1**, and almost all *p*-bromophenyl groups in P(*p*-BrSt) reacted with **1**. GPC data suggest that no significant decomposition of polymer backbone occurs. The Pd-catalyzed aryl amination is considered to involve β-hydrogen elimination reaction of the Pd intermediate,[4a−d] however, use of a diaryl secondary amine such as **1** would suppress the undesirable side reaction. In contrast to P(*t*-Bu)$_3$, other phosphine ligands were less effective, although tri-*o*-tolylphosphine [P(*o*-tolyl)$_3$] and 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (BINAP) have been found to be efficient for the Pd-catalyzed polycondensation.[5a,b] The polymer reaction did not proceed in the absence of the Pd catalyst. The introduction of an aminoazobenzene group into P(*p*-BrSt-*co*-St) was also smoothly carried out to afford Poly-**3** with almost quantitative DS value.

Table 2 summarizes the results of the Pd-catalyzed polycondensation of 1,3-dibromobenzene or bis(4-bromophenyl) ether with **2** using various catalyst systems. The molecular weights of the polymers were calibrated by GPC.[11] As shown in Table 2, use of P(*t*-Bu)$_3$ was also essential for the polycondensation to give the corresponding polymers in high yields, while use of other phosphine ligands such as P(*o*-tolyl)$_3$, BINAP, and 1,1′-bis(diphenylphosphino)ferrocene (DPPF) was less effective and afforded lower yields and lower molecular weights of the polymer. In our previous study, BINAP has been the most effective ligand for the polycondensation of 1,3-dibromobenzene with 1,3-phenylenediamine or 3-bromoaniline to afford poly(*m*-aniline).[5a] These results suggest that the combination of Pd$_2$(dba)$_3$ and P(*t*-Bu)$_3$ could serve as the effective catalyst for the amination of aryl bromides with secondary diarylamines to give triarylamines.[4h] Use of Cs$_2$CO$_3$, which has been found to be an appropriate base for the Pd-catalyzed amination,[4i,j] did not gave the polymer. The polycondensation of bis(4-bromophenyl) ether with **2** also afforded Poly-**4** in a good yield.

Characterization. Poly-**1**−**3** are soluble in CHCl$_3$, toluene, dioxane, *N*,*N*-dimethylformamide (DMF), and *N*,*N*-dimethylacetamide (DMAc), while Poly-**4** is soluble in CHCl$_3$, toluene, dimethyl sulfoxide (DMSO), and DMAc but partially soluble in DMF.

Figure 1 shows ^{1}H and ^{13}C NMR spectra of Poly-**1** (run 1 in Table 1) in CDCl$_3$. Assignment of the peaks was carried out by comparison of the peak positions of Poly-**1** with those of Model-**1**. In Figure 1a, the ratios of the peak area agree with the suggested assignment, and no peak assigned to the N−H proton (δ 6.0 ppm for **1**) is observed. IR spectrum of Poly-**1** is essentially the same as that of Model-**1**, and disappearance of the ν(C−Br) band [1074 cm^{-1} for P(*p*-BrSt)] and ν(N−H) band (3385 cm^{-1} for **1**) is observed. The ^{1}H NMR spectrum of Poly-**3** in CDCl$_3$ was also similar to Figure 1a, and the DS value estimated from ratios of the peak area almost agreed with the DS value determined by elemental analysis.

NMR data of Poly-**2** and Poly-**4** are also reasonable for their structures and indicate well-regulated structures. Figure 2 shows ^{1}H and ^{13}C NMR spectra of Poly-**2** (run 1 in Table 2) in CDCl$_3$. In Figure 2a, the ratios of the peak area agree with the suggested assignment, and no peak assigned to the N−H proton (δ 4.0 ppm for **2**) is observed. IR spectrum of Poly-**2** is also essentially the same as that of Model-**1**, and disappearance of the ν(C−Br) band (1075 cm^{-1} for 1,3-dibromobenzene) and ν_{as}(N−H) and ν_s(N−H) bands (3478 and 3382 cm^{-1} for **2**) is observed.

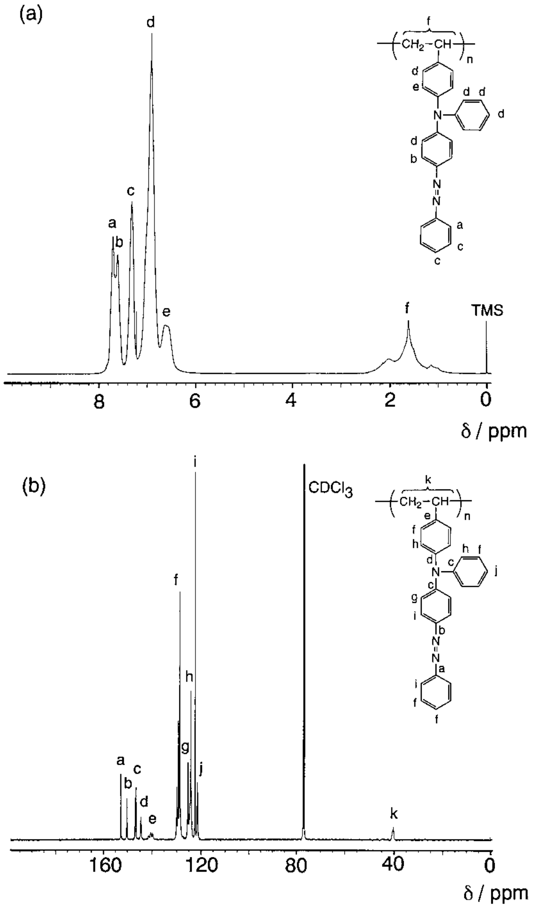


Figure 1. ^{1}H (a) and ^{13}C (b) NMR spectra of Poly-**1** in CDCl$_3$.

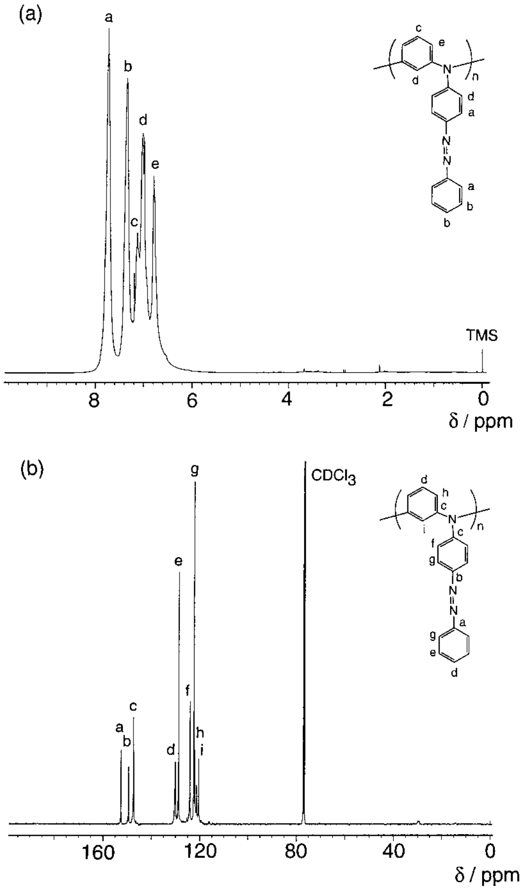


Figure 2. ^{1}H (a) and ^{13}C (b) NMR spectra of Poly-**2** in CDCl$_3$.

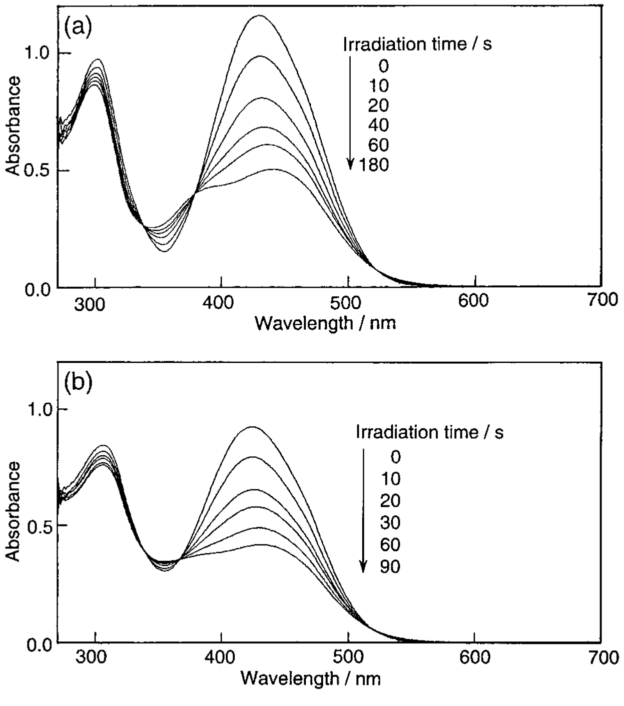


Figure 3. Changes in the absorption spectra of Poly-**1** (a) and Poly-**2** (b) (ca. 5 × 10^{-5} M of the azobenzene unit in DMAc) during irradiation with light at about 405 nm.

Thus, the elemental analyses and IR and NMR data indicate that the Pd-catalyzed polymer reaction and polycondensation provide the proposed polymers having the azobenzene group in their side chains.

Photoinduced and Thermal Cis–Trans Isomerization. The UV–vis absorption spectrum of Poly-**1** in DMAc exhibits two absorption peaks at 304 and 430 nm, presumably based on the π–π^* transitions of phenyl and aminoazobenzene units, respectively. The absorption spectrum is essentially the same as those of Model-**1** and Poly-**2**–**4**. Figure 3 shows changes in the absorption spectra of DMAc solutions of Poly-**1**,**2** during irradiation of light at about 405 nm. As shown in Figure 3, the absorption peak at 430 nm gradually decreased with light irradiation time with three isosbestic points at about 340, 380, and 525 nm due to the trans→cis photoisomerization of the azobenzene moieties in their side chains. When the samples irradiated at about 405 nm were annealed at 60 °C in the dark, the absorption peak at 430 nm steadily increased to the starting value before irradiation, indicating that the cis→trans isomerization of the azobenzene groups occurred thermally. Similar changes in the absorption spectra of the DMF and/or DMAc solutions of Model-**1** and Poly-**3**,**4** as well as cast films of Poly-**1**–**4** were also observed, respectively. In all samples, the photoinduced and thermal cis–trans isomerization was induced repeatedly, and no significant influence of solvents was observed on the azobenzene cis-trans isomerization.

Figure 4a shows a typical example of the plot for the thermal cis→trans reversion of the azobenzene group in Poly-**1** kept in the dark at 50 °C after light irradiation (5 min at about 405 nm). The thermal cis→trans isomerization of the azobenzene group obeyed first-order kinetics (Figure 4b), and the slope of plots of ln(A_∞ − A_t) (where A_t and A_∞ are absorbances at 430 nm at time t and infinite time, respectively) against time gave the first-order rate constants (k_T) for the thermal cis→trans

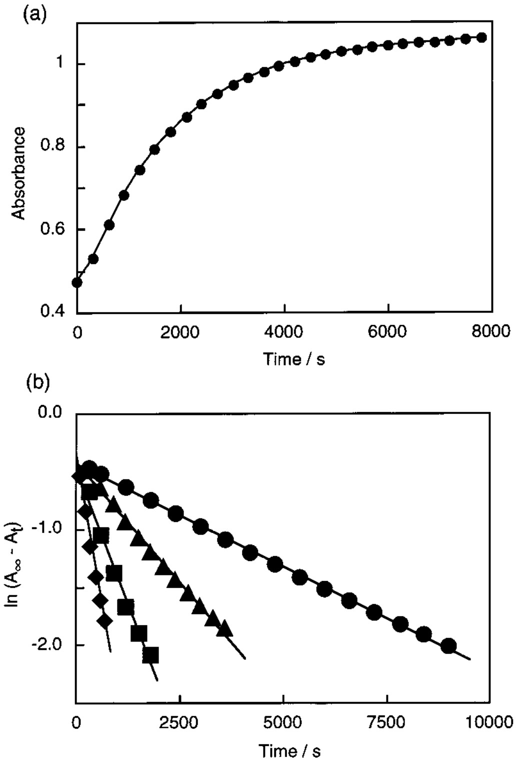


Figure 4. (a) Plot of absorbance at 430 nm of Poly-**1** (ca. 5 × 10^{-5} M of the azobenzene unit in DMF) kept in the dark at 50 °C after irradiation with light (at about 405 nm for 5 min); (b) First-order rate constant plots for cis→trans isomerization of the azobenzene group in Poly-**1** (●) at 40 °C, (▲) 50 °C, (■) 60 °C, and (◆) 70 °C.

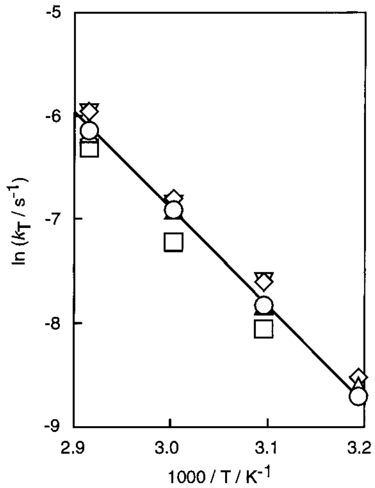


Figure 5. Arrhenius plots for the thermal cis→trans isomerization rates (k_T) of (○) Model-**1**, (△) Poly-**1**, (□) Poly-**2**, (◇) Poly-**3**, and (▽) Poly-**4**.

isomerization of azobenzene group.[1b,f,m] The thermal isomerization behaviors of Poly-**2**-**4** and Model-**1** also obeyed the first-order kinetics in DMF and/or DMAc. Figure 5 shows Arrhenius plots of k_T data of Poly-**1**–**4** and Model-**1**. From the slope of these plots, we estimated activation energy values (E_a) of about 18–19 kcal mol^{-1} for all samples. The E_a values are similar in magnitude to those of other azobenzene derivatives and polymers containing azobenzene groups.[1b,c,j,l,m] First-order kinetics was also observed for the photoinduced trans→cis isomerization of Poly-**1**–**4** and Model-**1** in DMF and/or DMAc as well as in the film state to give the photoisomerization rate constants (k_{obs}).

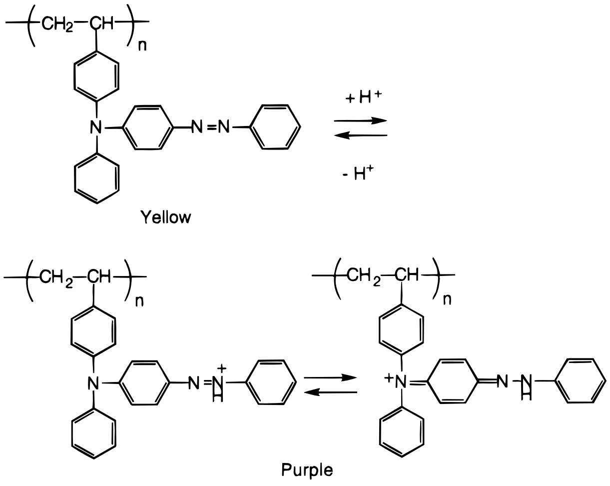
Table 3. Kinetics Data of the Isomeriazation of Azobenzene Moieties in Polymers and Model-1

run	sample	k_{obs}[a] × 10^2/s^{-1}	$k_{obs(film)}$[b] × 10^3/s^{-1}	k_{323K}[c] × 10^4/s^{-1}	E_a[d]/kcal mol^{-1}
1	Poly-**1**	3.5	8.0	4.2	18
2	Poly-**2**	3.6	8.0	3.2	19
3	Poly-**3**	3.6	8.0	5.0	18
4	Poly-**4**	3.3	8.0	5.0	18
5	Model-**1**	3.4		4.0	18

[a] Trans→cis photoisomerization rate constant under irradiation at about 405 nm in DMAc at room temperature. [b] Trans→cis photoisomerization rate constant of film under irradiation at about 405 nm. [c] Cis→trans thermal isomerization rate constant in DMF (runs 1, 3, and 5) and in DMAc (runs 2 and 4) kept in the dark at 50 °C. [d] Evaluated from Arrhenius plot of k_T.

Table 3 summarizes the kinetics data (k_T, k_{obs}, and E_a) of Model-**1** and the polymers in the solution and in the film state. As shown in Table 3, little difference is observed for k_T, k_{obs}, and E_a data between the polymers and Model-**1**. These data indicate that there is no significant influence of the structure of the polymer main chains such as the stiffness and steric factors of the polymer backbone on the azobenzene cis–trans isomerization in the solution as well as in the film state, although Poly-**2**,**4** having an imino-1,3-phenylene main chain are considered to take a more rigid helical structure than Poly-**1**,**3** with a random coil structure. The same tendency has been observed for the other polymers containing azobenzene group in the side chains.[1c,d,f,j,m] These results suggest that both thermal and photoinduced isomerization processes would occur by in-plane translation of the benzene ring further from the main chain rather than by rotation around the N=N bond.[1c,d]

Protonation. The absorption properties of the polymers and Model-**1** are also dependent on the acidity of the media. Figure 6 shows the changes in the absorption spectra of $CHCl_3$ solutions of Poly-**1**,**4** with increasing concentration of CF_3COOH. In Figure 6a, addition of CF_3COOH led to a decrease of the bands at 304 and 430 nm and an appearance of a new band at 550 nm with two isosbestic points at about 355 and 480 nm. $CHCl_3$ solutions of Poly-**2**,**3** and Model-**1** also display similar changes in the absorption spectra upon adding CF_3COOH. The new band at 550 nm may be assigned as the protonated resonating form of aminoazobenzene group analogous to that of Methyl Orange expressed by eq 6.[12]



(6)

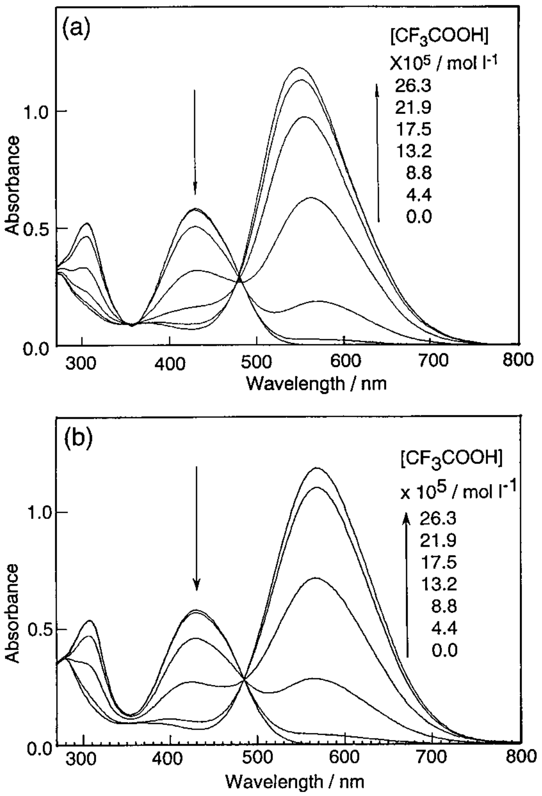


Figure 6. Changes in the absorption spectra of Poly-**1** (a) and Poly-**4** (b) (ca. 2.5 × 10^{-5} M of the azobenzene unit in $CHCl_3$) with increasing concentration of CF_3COOH.

Conclusion

The introduction of aminoazobenzene structure into the side chain of polystyrene smoothly proceeded by the Pd-catalyzed amination. The Pd-catalyzed polymer reaction could provide a variety of functional polymers by changing the structures of polymer-bound aryl bromides and amines. The Pd-catalyzed polycondensation of aryl dibromides with aminoazobenzene also afforded poly(iminoarylene)s having an azobenzene group in the side chain. Although poly(N-arylaniline) derivatives have been prepared by the Pd-catalyzed polycondensation of aryl dibromides with secondary aromatic diamines or N-substituted bromoaniline,[5b,c] the polycondensation of aryl dibromides with primary amines could provide a variety of poly(iminoarylene)s having functional substituent groups in the side chains in an one-pot procedure by changing the structure of aryl dibromides and primary amines.[13] The obtained polymers exhibited photoinduced and thermal isomerization properties of the azobenzene moieties; however, it appears that the structure of the polymer main chain has little effect on the isomerization behavior. The absorption properties of the polymers were also dependent on the acidity of the media. The chromic characteristics may provide new sensory devices.

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