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Organosilicon Polymers with Alternating σ- and π-Conjugated Systems

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A series of organosilicon polymers containing polysilane and diethynylaryl units along the polymer backbone were synthesized and examined with respect to their optical absorptions. The results indicate that delocalization takes place through the σ–π conjugated system. Lengthening of π-conjugation leads to lower excitation energies while nearly identical UV–vis spectra are observed with increased Si–Si chain length. Introducing a thiophene unit into the π-system instead of a benzene unit leads to a bathochromic shift reflecting greater σ–π delocalization. The polymers undergo photodegradation, probably via cleavage of the Si–Si bonds, and thermal crosslinking by reaction at the C≡C triple bonds. When doped with iodine, these polymers become semiconducting with conductivity of the order of 10^{-4} S cm^{-1}.

Keywords: organosilicon, polymers, semiconducting

INTRODUCTION

Organosilicon polymers containing alternating oligosilylene and an unsaturated carbon chain in the backbone represent a new class of electroactive polymers which display a great variety of intriguing properties such as photosensitivity,[1] conductivity[2] and nonlinear optical properties.[3] In addition these polymers can be used as precursors to silicon carbide ceramics.[4] Electron delocalization is known to take place involving the π-electrons of conjugated polymers and the σ-electrons in polysilanes, but little is yet known about the interactions between the σ and π systems in polymers containing both kinds of conjugation.[5] In this paper, we examine organosilicon polymers possessing various σ- and π-conjugated lengths with regard to their electronic absorptions, conductivities upon doping of iodine, and photo and thermal stability.

EXPERIMENTAL SECTION

Proton NMR spectra were recorded on a Bruker WP-200SY FT spectrometer from C_6D_6 solutions. ^{13}C and ^{29}Si NMR spectra were obtained using a Bruker AM-500 spectrometer. Electronic absorption spectra were measured in tetrahydrofuran (THF) with a Perkin-Elmer Lambda Array 3840 UV–vis spectrometer. Infrared spectra were obtained from cast thin films on sodium chloride pellets and recorded on a Polaris FT–IR spectrometer. Thermal analysis was conducted by using a differential scanning calorimeter (Perkin–Elmer DSC-7), routinely calibrated with mercury, indium and zinc standards, at a heating rate of 20 °C min^{-1}. A Waters 6000A solvent delivery system equipped with a series of four microstyragel columns (10^3, 10^4, 10^5 and10^6 Å) was used for gel permeation chromatography analysis. Analysis was performed by using THF as the eluent at a flow rate of 1.5 ml min^{-1}. Molecular weights are calibrated relative to polystyrene standards. The conductivity measurements were carried out using the four-probe method with gold electrodes at room temperature. The polymer films, prepared by spin coating on a glass substrate from the corresponding THF solution, were exposed to iodine vapor in an evacuated chamber and the reading of conductivity was taken simultaneously.

The precursors, α,ω-diethynyloligosilylenes,[6] were prepared by coupling of the corresponding dichlorooligosilylene and ethynyl magnesium bromide in THF. The monomer of 1,4-diethynylbenzene was synthesized via the debromination of 1,4 bis(1,2-dibromoethyl)benzene as has been detailed in several articles.[7] The p-diiodobenzene and 1,4-diiodothiophene were used as received from Aldrich Chemical Co. without further purification. A polymerization procedure typical of that used for preparing all of the polymers is given here.

Polymer **1a**: a mixture of 1,2-diethynyl-1,1,2,2-tetrabutyldisilane (1.34 g, 4 mmol), 1,4-diiodo-

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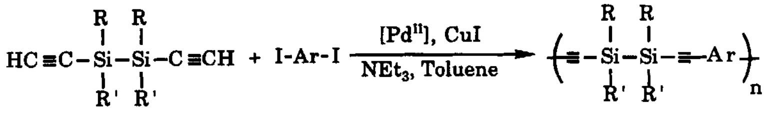
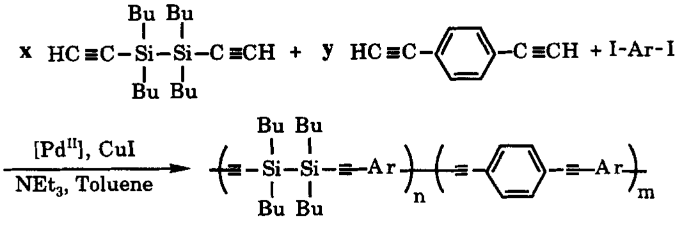


1a: R = R' = n-Bu, Ar = Benzene

1b: R = Ph, R' = Me, Ar = Benzene

1c: R = R' = n-Bu, Ar = Thiophene



x + y = 1

3a: Ar = Benzene, x/y = 1

3b: Ar = Benzene, x/y = 3

3c: Ar = Thiophene, x/y = 1

Scheme 1

benzene (1.32 g, 4 mmol), CuI (4×10^{-5} mol, 7.6 mg), and $(PPh_3)_2PdCl_2$ (4×10^{-6} mol, 2.8 mg) were dissolved together in 30 ml of toluene. After addition of *ca* 5 ml of NEt_3, the reaction mixture was stirred for 10 h at ambient temperature, then refluxed for 12 h. Quantitative precipitation of Et_3NHCl salt was observed during the reaction. After cooling the reaction mixture, the precipitates were removed by passing through a short silica gel column. The solvent was pumped off and 50 ml of THF was added to dissolve the residue, which was filtered again. The resulting filtrate was added to excess methanol with stirring to precipitate the polymer. The precipitate was dried under vacuum for 48 h and gave a red elastomer (1.05 g, 65%).

RESULTS AND DISCUSSION

The series of organosilicon polymers were prepared by catalytic polymerization (the Heck reaction)[8] as shown in Scheme 1. The structure of the model polymer **1a** was determined spectroscopically by carbon and silicon NMR spectra. In ^{29}Si NMR spectrum shown in Fig. 1, a sharp peak at −32.7 ppm is ascribed to a simple nuclear environment of silicon in the polymer chain. Four well-defined resonances observed in the ^{13}C spectrum (Fig. 1) are assigned to two *sp* carbons (93.8 and 108.0 ppm) and sp^2 carbons (123.3 and 131.6 ppm). These data are consistent with the expected structure in which the polymer backbone is a regular alternating arrangement of disilylene and 1,4-diethynylbenzene units.

In our previous investigation of poly(ethynylene-co-disilylene),[9] a red shifted electronic absorption at 240 nm was observed relative to the corresponding monomeric species $HC{\equiv}(SiMe_2)_2C{\equiv}CH$ (217 nm), attributed to σ–π delocalization. Similarly, the absorption band of polymer **1a** at 298 nm is significantly red-shifted compared to those for the monomers, $HC{\equiv}C(SiBu_2)_2C{\equiv}CH$ (219 nm) and $HC{\equiv}CC_6H_4C{\equiv}CH$ (264 nm), indicating extensive electron delocalization in the polymer chain. Undoubtedly, the disilylene unit in the structure of polymer **1a** acts as an electroactive segment; the extended delocalization of π-electrons through the disilylene leads to a lower electronic transition energy.

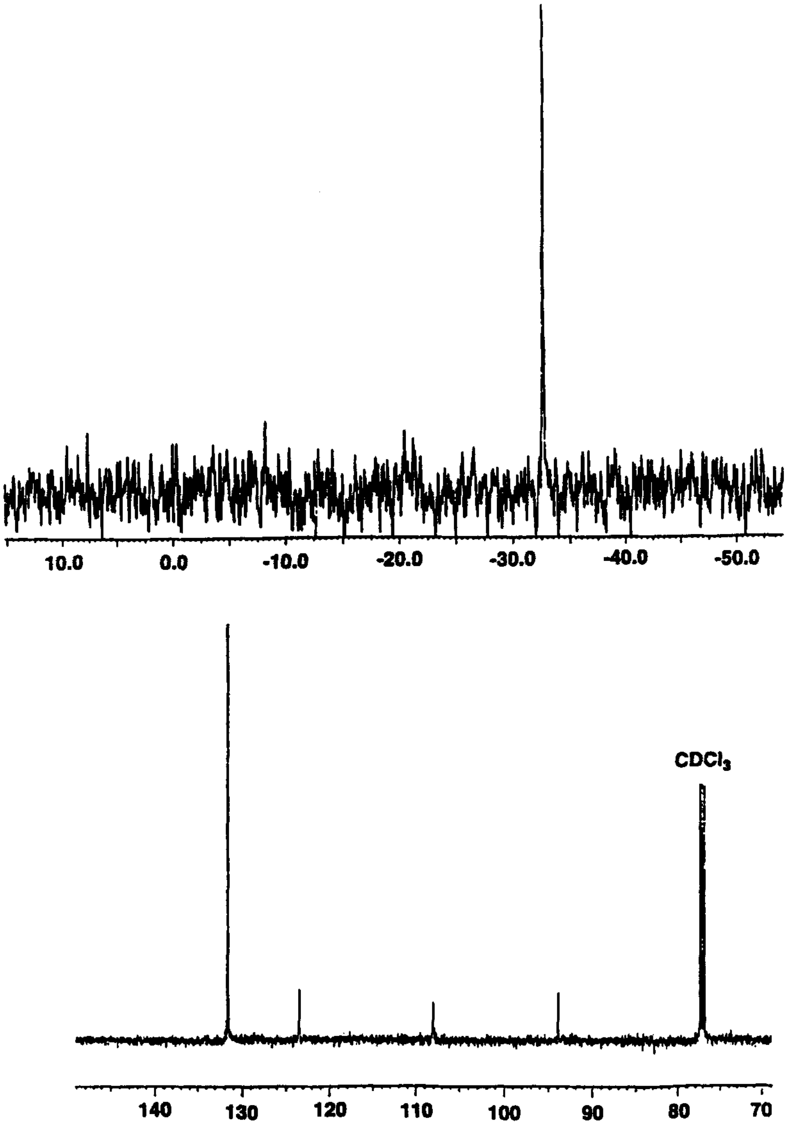


Figure 1 ^{29}Si NMR (top) and ^{13}C (bottom) spectra of polymer **1a** in CDCl$_3$.

Polymers analogous to polymer **1a** but with different pendent *n*-alkyl groups (*n*-alkyl = propyl and hexyl) gave UV absorption bands identical to that of polymer **1a**. In aryl-substituted polysilanes and disilanes,[10] lowering of the optical energy gap is often observed, resulting from the interaction of Si–Si σ orbitals and aryl π orbitals. To probe the influence of an aryl substituent on silicon in these polymers, a 1,2-dimethyl-1,2-diphenyldisilylene moiety was introduced into the backbone in place of the tetraalkyldisilylene units. The UV absorption of polymer **1b** seen in Table 1 shows no significant difference from those of the alkyl analogs. Evidently, the electronic structure of this organosilicon polymer system, unlike the polysilanes, is relatively independent of the nature of substituents on silicon.

Next, we investigated the influences of the length of the σ- and π-conjugated segments embedded in polymer main chain. Reducing the number of silicons from two to one, in polymer **2a**, decreases through-conjugation as shown by the 18 nm blue shift (Table 2). Increasing the number of silicons beyond two, as in polymer **2b** and **2c**, does not change the absorption wavelength much. (An additional band at higher

Table 1

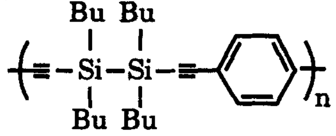
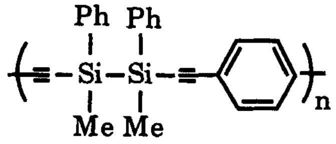
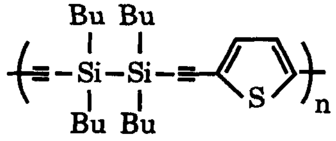
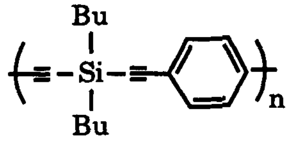
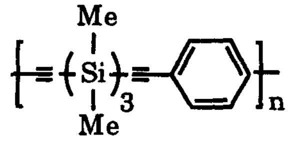
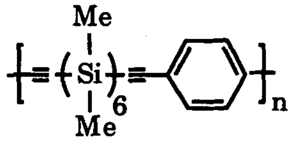
Polymer	Polymer Unit	M_w	λ_{max} (nm)
1a		28,800	298
1b		31,000	297
1c		12,700	325

Table 2

Polymer	Polymer Unit	M_w	λ_{max} (nm)
2a		27,800	280
2b		44,300	290
2c		10,700	266,294

energy is found for polymer **2c**, assigned to the hexasilane chromophore.) Apparently, the effect of the lower σ–σ^* excitation energy, resulting from extending the σ-conjugated unit beyond disilylene, does not greatly affect the σ–π delocalization.

Copolymerization of diethynylbenzene with

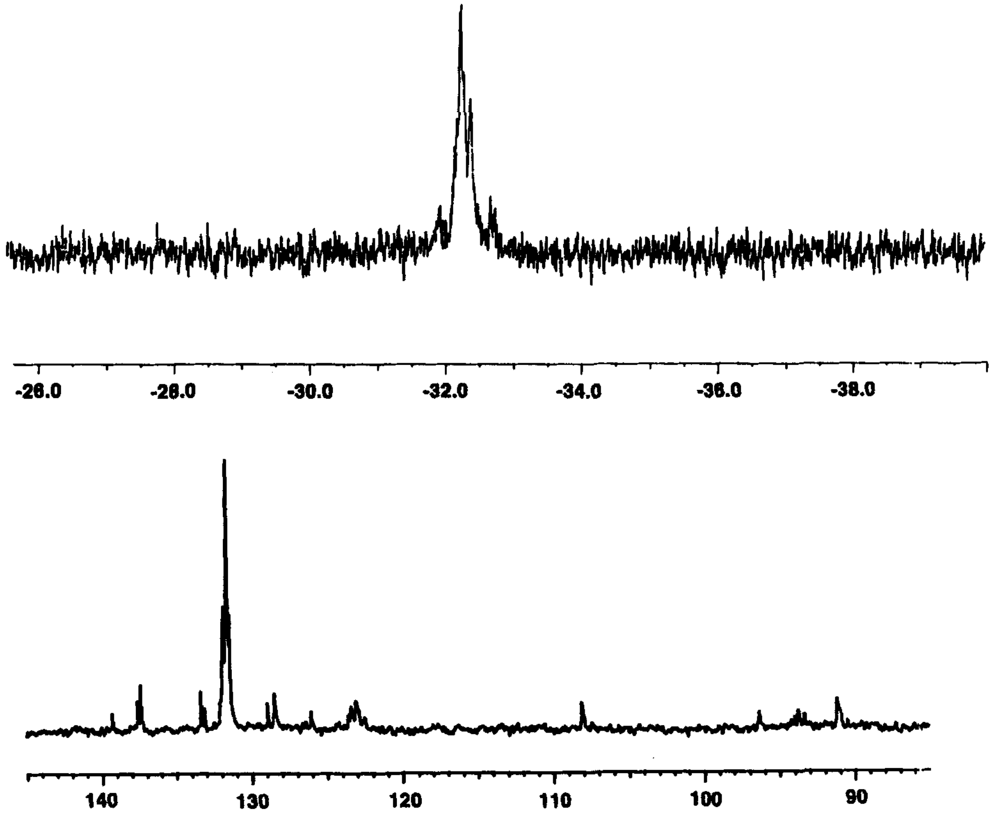
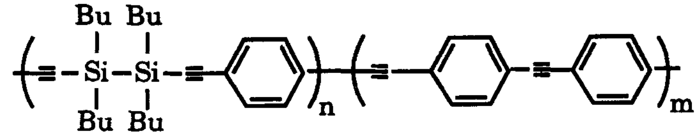
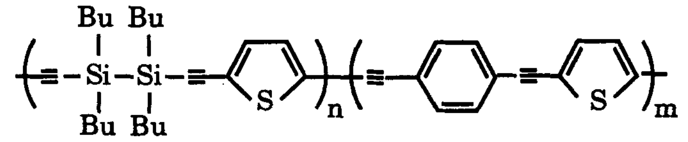


Figure 2 ^{29}Si NMR (top) and ^{13}C (bottom) spectra of polymer **3a** in $CDCl_3$.

Table 3

Polymer	Polymer Unit	M_w	λ_{max} (nm)
3a		117,500	311,346,365
3c		27,300	346,382,400

$HC{\equiv}C(SiBu_2)_2C{\equiv}CH$ and *p*-diiodobenzene generated copolymers **3a** and **3b**, containing segments with longer π-conjugation, as illustrated in Scheme 1. Each of the nuclear resonances in the carbon and silicon NMR spectra for polymer **3a** is a multiplet (Fig. 2), in contrast to the well-defined sharp peaks observed for polymer **1a**. This result suggests a statistical arrangement of σ and π segments along backbone. The ratio of σ and π units in the polymer structure corresponds approximately to the mixing ratio of monomers, according to the proton NMR spectrum. The UV spectra of polymers **3a** and **3b** exhibit two bands at 311 and 346 nm as well as a shoulder at 365 nm (Fig. 3). Polymers **3a** and **3b** must possess longer π-conjugated moieties, i.e. $—C{\equiv}C—(C_6H_4C{\equiv}C)_3—$ or $—C{\equiv}C—(C_6H_4C{\equiv}C)_4—$, not present in polymer **1a**. Therefore, the 346 and 365 nm absorption bands observed in polymer **3a** and **3b** can be attributed to the chromophores containing longer π-conjugated segments, while the 311 nm band is assigned to a red-shifted

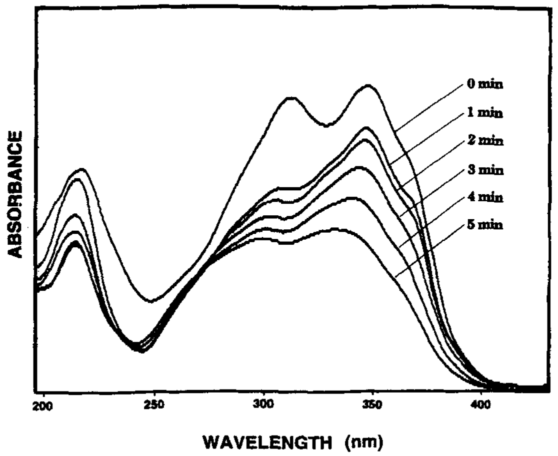


Figure 4 Bleaching of polymer **1a** in THF upon irradition at 300 nm.

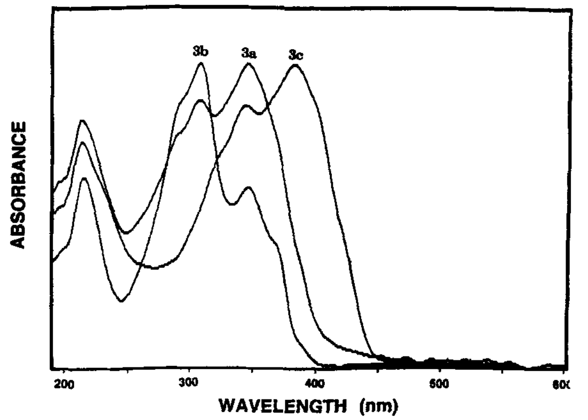


Figure 3 UV–vis spectra of polymers **3a**, **3b** and **3c** in THF.

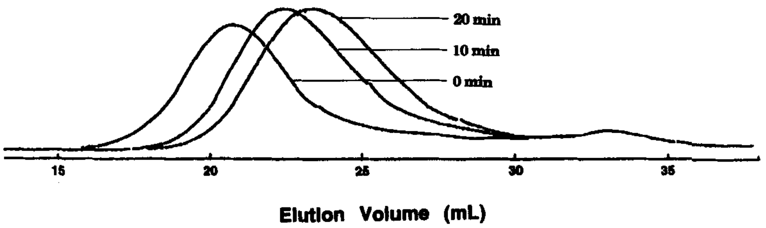


Figure 5 GPC traces of polymer **3a** in THF after (a) 0 min, (b) 10 min, and (c) 20 min irradiation.

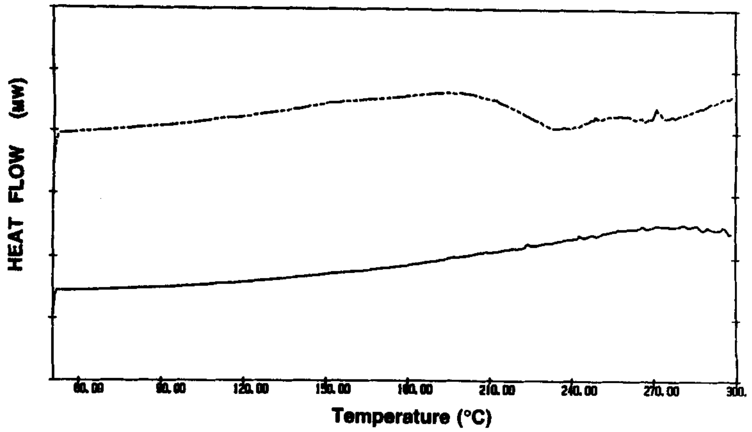


Figure 6 DSC thermograms of polymer **3a** at the first heating scan (top) and second heating scan (bottom).

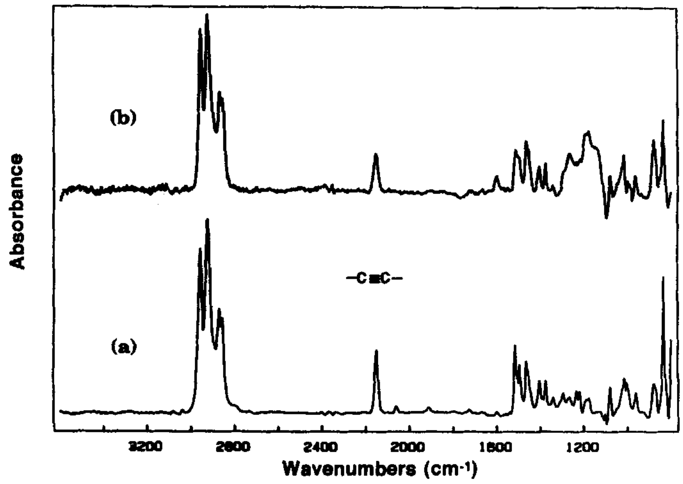


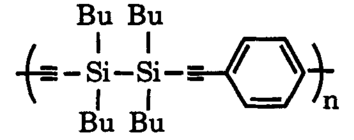
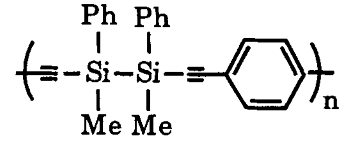
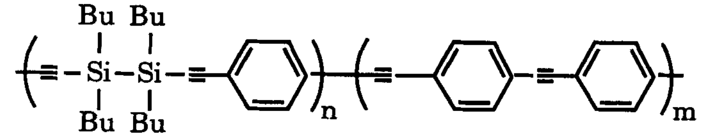
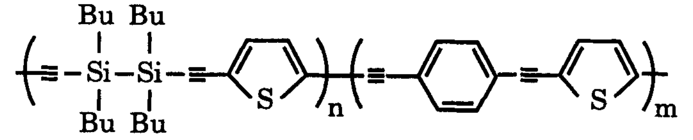
Figure 7 FTIR of polymer **3a** (a) before and (b) after thermal treatment for 48 h at 200 °C.

absorption of the segment with arrangement of polymer **1a**. The spectra of polymers **3a** and **3b** are similar, but in **3b**, which contains a smaller number of diethynylbenzene units, the peaks at 346 and 365 nm are less intense, as expected since the number of long π-conjugated segments are decreased.

In polymer **1c**, a thiophene ring is present in place of the benzene unit in polymer **1a**. The absorption maximum for **1c** is strongly red-shifted at 325 nm. Similarly, the electronic absorption of polymer **3c**, which contains thiophene rings, shows a red-shifted pattern (Fig. 3; Table 3) compared to the UV specrum of polymer **3a**. It is clear that the electronic structure of these organosilicon polymers is strongly dependent on the π-conjugated moieties.

Photolysis of polymer **1a** in THF solution leads to bleaching of the UV absorption bands (Fig. 4). The bleaching experiment was followed by size exclusion chromatography (Fig. 5) showing a continuous decrease in molecular weight with the exposure time. Photodegradation caused by the homolytic scission of Si–Si bonds is a characteristic feature of catenated silicon chains and this is possibly the mechanism for the reduction of molecular weight of polymer **1a** upon irradiation.[11] In this class of polymers,[1] polysilylene units may provide the active sites for photoscission reactions. The acetylene groups, on the other hand, are susceptible to thermal crosslinking. The thermogram of polymer **3a** (Fig. 6) shows an exothermic reaction with onset at about 190 °C. This exotherm vanishes in the second heating run,

Table 4

Polymer	Polymer Unit	Conductivity (S/cm^{-1})	Film Thickness (μm)
1a		5.6×10^{-5}	1.0
1b		1.2×10^{-4}	0.5
3a		$1.0. \times 10^{-4}$	1.0
3c		5.3×10^{-4}	0.2

which suggests that the crosslinking is complete during the first heating. The IR spectra (Fig. 7) confirm that crosslinking takes place during the thermal reaction. The characteristic —C≡C— stretching at 2150 cm^{-1} gradually decreases as the polymer is kept at 200 °C, and no significant siloxane band appears in the region 1150–1000 cm^{-1}.

From the conductivity data shown in Table 4, the iodine-doped polymer films are in the semiconductive range of 10^{-4} S cm^{-1}. Higher conductivity of polymers having longer π-conjugated length is consistent with the enhancement of σ–π delocalization associated with a smaller energy gap. Among these polymers, polymer **3c** shows the greatest conductivity and the strongest σ–π delocalization.

In conclusion, investigations of the electronic absorption of these polymers covering the range of substituents, and the length of σ-conjugated and π-conjugated segments have demonstrated that the contribution of π-conjugation dominates the σ–π delocalization. We also observed a significant enhancement of delocalization as the thiophene is inserted into the backbone.

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REFERENCES

1. S. S. Hu and W. P. Weber, *Polym. Bull.* **21**, 133 (1989). (b) M. Ishikawa, H. Ni, H. Watanabe and Y. Saheki, *Organometallics* **6**, 1673 (1987).
2. (a) J. Ohshita, D. Kanaya, M. Ishikawa, T. Koike and T. Yamanaka, *Macromolecules* **24**, 2106 (1991). (b) R. Corriu, C. Guerin, B. Henner, T. Kuhlmann, A. Jean, F. Garnier and A. Yassar, *Chem. Mater.* **2**, 351 (1990).
3. R. Corriu, W. E. Douglas, Z. X. Yang, Y. Karakus, G. H. Cross and D. Bloor, *J. Organometal. Chem.* **455**, 69 (1993).
4. (a) R. Corriu, P. Gerbler, C. Guerin, B. Henner, A. Jean and P. H. Mutin, *Organometallics* **11**, 2507 (1992). (b) H. J. Wu and L. V. Interrante, *Macromolecules* **25**, 1840 (1992).
5. (a) R. West, S. Hayase and T. Iwahara, *J. Inorg. Organomet. Polym.* **4**, 42 (1991). (b) J. Wildeman, J. K. Herrema, G. Hadziioannou and E. Schomaker, *J. Inorg. Organomet. Polym.* **4**, 567 (1991).
6. W. Wojnowski, C. J. Hurt and R. West, *J. Organomet.*

Chem. **124**, 271 (1977).

7. (a) A. S. Hay, *J. Org. Chem.* **25**, 637 (1960). (b) F. Siebzehnrubl and O. Nuyken, *Macromol. Chem.* **189**, 541 (1988).
8. (a) H. A. Dieck and F. R. Heck, *J. Organomet. Chem.* **93**, 259 (1975). (b) L. Cassar, *J. Organomet. Chem.* **93**, 253 (1975).
9. T. Iwahara, S. Hayase and R. West, *Macromolecules* **23**, 1298 (1990).
10. (a) H. Shizuka, H. Obuchi, M. Ishikawa and M. Kumada, *J. Chem. Soc., Chem. Commun.* 405 (1981). (b) H. Shizuka, Y. Sato, Y. Ueki, M. Ishikawa and M. Kumada, *J. Chem. Soc., Faraday Trans. (1)* **80**, 341 (1984).
11. (a) P. Trefonas, R. West, R. D. Miller and D. Hofer, *J. Polym. Sci., Polym. Lett. Ed.* **21**, 823 (1983). (b) P. Trefonas, R. West and R. D. Miller, *J. Am. Chem. Soc.* **107**, 2737 (1985).