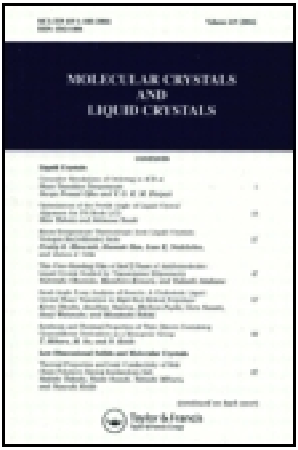

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Novel Electrical and Optical Properties of Substituted Conducting Polymers

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NOVEL ELECTRICAL AND OPTICAL PROPERTIES OF SUBSTITUTED CONDUCTING POLYMERS

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Abstract Drastic change of properties of conducting polymer by substitution of side group has been demonstrated utilizing poly(3-alkylthiophene) as s typical example. Electrical (conductivity, mobility) and optical (absorption, luminescence) properties of poly(3-alkylthiophene) were strongly dependent on alkyl chain length, temperature and ambient conditions. These results can be explained by taking account fluctuation of electronic band scheme and change in inter-chain interaction which are dependent on the alkyl chain length and its conformation. Properties of mixture of poly(3-alkylthiophene)s with different alkyl chain length were also discussed. Doping characteristics of poly(3-alkylthiophene) dependent on alkyl chain length were discussed in terms of modification of crystal structure, location of dopants, and polymer-dopant interaction. Especially, unique doping effect of C60 in poly(3-alkylthiophene) such as photo-induced charge transfer was also observed.

Characteristics of poly(3-alkylthiophene) in solvent and behavior of poly(3-alkylthiophene) gel were studied and discussed in terms of interactions of solvent molecule with both polymer main chain and alkyl side chain. Various applications of these unique characteristics of poly(3-alkylthiophene) were proposed, functional electronic element (diodes, FET etc.), EL (electroluminescent diode), photo-conductive and photo-voltaic elements, optical memory and functional gel elements (bimorph, actuator, etc.). Their characteristics can also be explained in terms of unique electronic band scheme of poly(3-alkylthiophene) dynamically dependent on alkyl chain length and ambient conditions.

INTRODUCTION

Since the discovery of insulator-metal transition upon doping in polyacetylene, conducting polymer whose main chains are composed of conjugated π bonds has attracted much attention from the fundamental physical viewpoints. Proposals of various applications of conducting polymers as a secondary battery[1], optical switching elements[2], electronics elements[3], sensor[4] etc. have also stimulated synthesis of new conducting polymers.

Small modification of molecular structure of conducting polymer results in drastic change in the properties of conducting polymer. Especially, substitution of conducting polymer with appropriate side groups results in the drastic change of its property. Among various substituted conducting polymers, poly(3-alkylthiophene) (PAT-n; n indicates alkyl chain length: $-C_nH_{2n+1}$) is one of the most interesting conducting polymer. By introducing of the most simple substituent, alkyl group, properties of polythiophene undergo drastic change. Here, we mainly discuss PAT-n as a representative of substituted conducting polymers. That is, recently developed conducting polymer PAT-n has been found to demonstrate fusibility[5] and drastic changes of electrical and optical properties depending on alkyl chain length, temperature, pressure, and atmosphere[6,7]. Recently, we have also found that non-soluble part of PAT-n exhibits unique functional gel characteristics[8,9].

In this paper, dependences of electrical conductivity, absorption spectrum and luminescence in PAT-n on alkyl chain length and temperature are studied by taking the change of crystal structure and polymer conformation depending on these factors into consideration. Effects of various dopants on their characteristics are also clarified. Novel optical and mechanical properties of conducting polymer gel and their dynamic behaviour are also discussed. Applications of these novel characteristics are also reported.

EXPERIMENTAL

PAT-n was prepared from corresponding 3-alkylthiophene by both chemical method utilizing $FeCl_3$ as a catalyst and also electrochemical polymerization. Details of preparation method of these polymer films were already reported in our previous papers[10-12]. Films were obtained by casting from chloroform solution of soluble PAT-n. Figure 1 indicates molecular structure of PAT-n.

PAT-n gel was also prepared from PAT-n film either by treat with BPO (benzoyl peroxide) or g-ray irradiation. Details of preparation were also reported in previous papers[13,14].

Electrical conductivity was measured by two and four probes methods. Optical absorption spectrum was measured utilizing a Hitachi 330 spectrophotometer. Photoluminescence spectrum was measured utilizing a photodiode and a lock-in amplifier

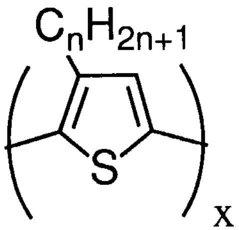

Figure 1 Structure of PAT-n

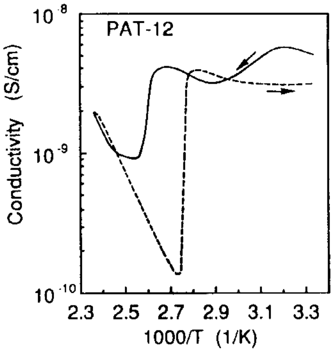

Figure 2 Temperature dependence of conductivity of PAT-12

(PAR117) system and also an Ar ion laser of 488 nm in wavelength as the exciting light source. Crystal structure was studied by Rigaku RINT 1100 system. Electrochemical properties were also studied utilizing HOKUTO DENKO HA-501 and HB-104.

RESULTS AND DISCUSSION

So far, conducting polymer has been considered to be non-fusible and non-soluble. However, we have found that upon introduction of long alkyl side chain conducting polymer becomes fusible at relatively low temperature[5,15]. Both melting point Tm and glass transition point Tg of PAT-n decrease with increasing alkyl chain length[16]. In the temperature between Tm and Tg, PAT-n exhibited various novel characteristics ;

(a) Anomalous temperature dependence of conductivity was observed in PAT-n as shown in Fig. 2. Conductivity increases with temperature but indicates peak at temperature between Tm and Tg. At Tm, conductivity drops in step wise and in the liquid state conductivity again increases with increasing temperature[17]. Conductivity decreases with increasing alkyl chain length.

(b) Thermochromism was observed in PAT-n as shown in Fig. 3. Absorption spectrum of PAT-n shows blue shift with increasing temperature. In the solid state below Tm, the absorption peak shifts to shorter wavelength with increase temperature but the absorption edge dose not change. At, Tm, the absorption edge also shows blue shift[17]. These thermochromic phenomena are reversible and are observed at lower temperature in PAT-n of longer alkyl chain length.

(c) Anomalous photoluminescence was observed in PAT-n as shown in Fig.4. Photoluminescence intensity is enhanced with increasing temperature and after indicating a peak at around Tm, it again decreases in the liquid phase[18]. Stronger luminescence was observed in PAT-n with longer alkyl chain.

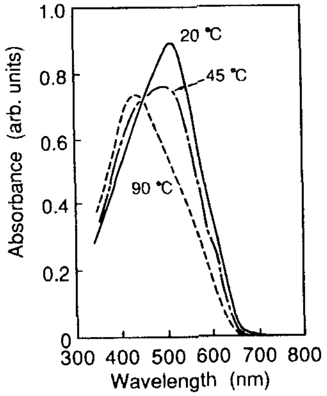

Figure 3 Temperature dependence of absorption spectrum of PAT-12

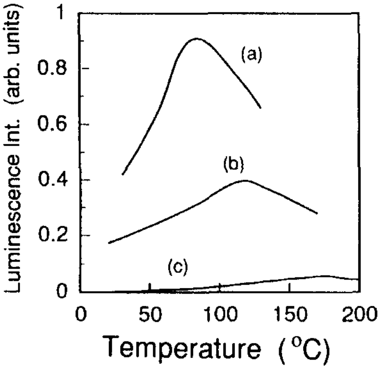

Figure 4 Temperature dependence of photoluminescence peak intensity of (a) PAT-22, (b) PAT-12, and (c) PAT-6.

These characteristics can be explained by the modification of electronic band scheme and change in inter-chain interaction induced by changes of co-planarity of the conjugated main chain which are dependent on alkyl chain and its conformation. That is, we have expected the longer inter-chain distance and decrease of co-planarity of thiophene rings on a main chain in PAT-n of longer alkyl chain and at high temperature, resulting in the larger band gap. We have carried out X-ray and IR measurements in PAT-ns of various alkyl chain length and at various temperature to confirm these speculations.

Crystal structure was confirmed to be orthorhombic in all PAT-n of various alkyl chain length. As shown in Fig. 5, lattice parameter *a* in the direction of alkyl chain increases with increasing alkyl chain length, tending to saturate. On the other hand, lattice parameter *b* is constant up to PAT-12 then increases for longer alkyl chain. These facts suggest that conformation of the alkyl side chain is in all-trans but for extremely long alkyl chain effects of trans-gauche conformation appear. By IR measurements, it was also confirmed that even in PAT-n of relatively short alkyl chain, trans-gauche conformation change occurs with increasing temperature. Appearance of bulky gauche conformation

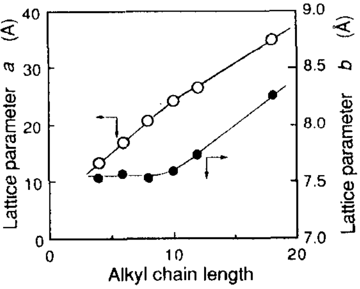

Figure 5 Dependence of lattice parameters of PAT-n on alkyl chain length.

induces steric hindrance between side chain and thiophene ring, resulting in the torsion of bonds between thiophene rings on a chain and fluctuation of electronic band scheme.

Fluctuation in the electronic band scheme in the pre-melting region can explain the anomalous temperature dependence of conductivity. Lower conductivity in PAT-n of longer alkyl chains can be explained by the decrease in carrier mobility and decreased probability of inter-chain carrier transfer on account of this fluctuation and longer inter-chain distance.

Fluctuation of electronic band scheme also explain the temperature dependence of absorption spectrum, thermochromism. Anomalous temperature and alkyl chain length dependences of the photoluminescence are explained by the confinement effect of photo-excited spices due to fluctuation of electronic band scheme and smaller inter-chain interaction. The mixture of PAT-ns of different alkyl chain length also exhibited unique properties.

Large spectral change of PAT-n by changing solvent (solvatochromism) was observed and can be explained by the change in electronic energy states due to conformational change of the main chain triggered by the change in alkyl chain conformation induced by the interaction with solvent molecule. In some cases, direct interaction exists between polymer main chain and solvent molecules. For example, we have found correlation between the spectral shift in PAT-n with Taft's π^* parameter of some solvent molecules which suggests the existence of electronic interaction between conjugated systems and solvent molecules.

Similar interaction was also confirmed in the study of dynamics of PAT-n gel. That is, we have found that PAT-n with appropriate densities of cross-linkings exhibits typical gel characteristics such as volume instability upon changing solvent and also

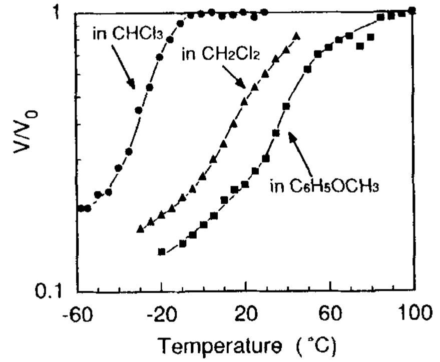

Figure 6 Volume instability of PAT-6 gel depending on temperature and solvent.

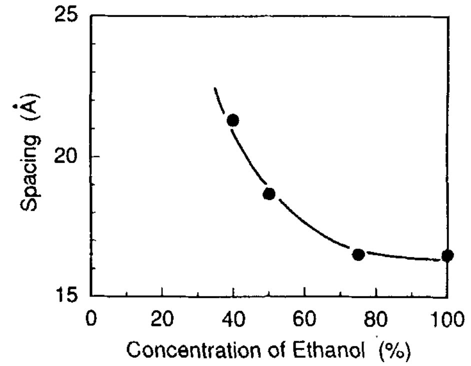

Figure 7 Dependence of inter-chain distance of PAT-6 gel on ethanol ratio of ethanol-chloroform solution.

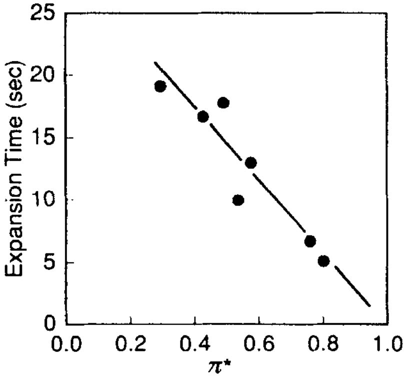

Figure 8 Dependence of expansion time of PAT-6 gel on the π^* parameter of solvent.

temperature as shown in Fig. 6. The absorption spectrum and the photoluminescence also changed associating with the volume instability. These unique gel characteristics can be explained by the change in conformation of polymer main chain and in inter-chain distance with solvent and temperature which is directly confirmed by X-ray diffraction measurements as shown in Fig. 7. It should also be stressed that the speed of volume change of PAT-n gel depends strongly on the kind of solvent molecule. The response time dose not depend on dielectric constant, size of molecule and also viscosity but it depends on Taft's π^*-parameter as shown in Fig. 8. This fact also suggests that the direct interaction between main chains and solvent molecules exists. Shrinkage of PAT-n gel was observed upon doping, which can be explained by the enhancement of inter-chain interaction by dopant.

PAT-n film can be effectively doped just as other conducting polymers. The existence of alkyl side chain also influences the doping characteristics. That is, the location of dopant in PAT-n and doping dynamics depend on the alkyl chain length.

We have found that upon doping inter-chain distance along *a*-axis of crystalline lattice increases but the inter-chain distance along *b*-axis of the crystalline lattice shrunk upon doping as shown in Fig. 9. This anomalous shrinkage can be explained by the enhancement in the inter-chain interaction due to the formation of quinoid like structure corresponding to polaronic states and also by the interaction assisted by the existence of dopants. We have found that dopant locates at a hexahedral type vacant space in the PAT-n lattice. When alkyl chain is relatively short, lattice spacing along *a*-axis must become longer to allow dopant molecule in this site upon doping. In the case of long alkyl side chain, it exhibits enough space for dopant and, therefore, adjustment of the crystal structure seems to be not necessary.

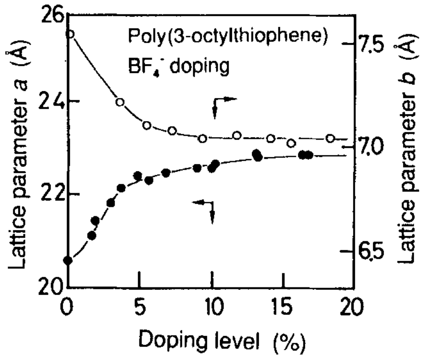

Figure 9 Dependence of lattice parameters of PAT-8 upon doping level of BF_4^-.

The existence of long alkyl side chain and large space in crystalline lattice of PAT-n allows doping of large dopants. For example, we have studied C60 doping in PAT-n. Indeed, change of absorption spectrum was observed upon C60 doping. However, the changes of electrical conductivity and ESR upon C60 doping were less remarkable compared with other conventional dopants. These facts indicate that C60 is a marginal dopant for PAT-n. On the other hand, it should be stressed that quenching of photoluminescence and remarkable enhancement in photoconduction were observed upon C60 doping. This can be interpreted by the photo-induced charge-transfer between PAT-n and C60. Photo-voltaic response was also observed utilizing this system.

Various applications utilizing unique characteristics of PAT-n sensitive to temperature and ambient conditions were proposed such as unique diodes, FET, sensors, EL diodes, actuators, photoconductor, photovoltaic device, optical recording, photocatalyst, etc.

Here, it has been demonstrated that even by the introduction of simple alkyl group as a substituent, PAT-n exhibits unique characteristics and various new applications can be possible. Introduction of other functional moiety as a substituent in various conducting polymers should results in the appearance of novel properties.

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