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Polymer 40 (1999) 995–1000

polymer

Characteristics of water in polypyrrole films

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Received 11 March 1998; accepted 20 April 1998

Abstract

Polypyrrole films containing different dopant ions were electrochemically synthesized and the interaction between polypyrrole and water was evaluated by means of sorption isotherm, cluster function and d.s.c. It was found that the water sorbed in the polypyrrole behaved as a non-freezing bound water which was rather isolated and prevented from clustering over the whole experimental range of the relative water vapour pressure from 0.1 to 0.95. This might be associated with the nature of the conductive polymers having a π-conjugated system where the delocalization of carbonium charges would lower the ionic polarity and hydrophilicity of the polymeric chains. © 1998 Elsevier Science Ltd. All rights reserved.

Keywords: Water in polypyrrole; Sorption isotherm; Cluster function

1. Introduction

It is well known that conductive polymers undergo dimensional changes on electrochemical or chemical doping and dedoping in an electrolyte solution [1,2]. The dimensional change is characterized by the transportation of solvated ions between the inside of the polymeric matrix and the surrounding electrolyte solution, and electrostatic repulsion and/or structural distortion through oxidation of polymers [3,4]. On the basis of this nature of conductive polymers, many studies have been made on preparing actuating devices owing to their potential applications to artificial muscles [5–8] or micromachines [9].

Previously, we reported that the electrochemically synthesized polypyrrole solid films underwent quick and intensive bending in ambient air [10,11] as a result of reversible sorption of water vapour, which causes a dimensional change of the film [12]. By using this phenomenon, we devised a new class of polymeric actuators driven by a free energy change of water vapour sorption [13]. Currently, we have discovered that the polypyrrole film exhibits a rapid contraction in ambient air by applying a d.c. voltage [14]. The mechanism is attributed to an electrically induced desorption of water vapour, which distinguishes it from electrochemical doping and dedoping [1–9].

Although the water plays a predominant role in causing a rapid and reversible conformational change of the polypyrrole, little is known about the states and characteristics of water sorbed in the polypyrrole film. We demonstrate here sorption isotherms and calorimetric measurements for various polypyrrole films with different dopant ions. Further, the results obtained were compared with those of poly(acrylic acid) as a typical polyelectrolyte.

2. Experimental

2.1. Materials

Pyrrole monomer was purified by distillation before use. The tetraethylammonium salts of tetrafluoroborate (BF_4^-), perchlorate (ClO_4^-), and tosylate (TsO^-) as electrolytes, and propylene carbonate as a solvent were commercially available and used without further purification. The tetraethylammonium salt of dodecylbenzenesulfonate (DBS^-) was synthesized by neutralization of dodecylbenzenesulfonic acid with an appropriate amount of tetraethylammonium hydroxide. Poly(acrylic acid), glycerin, and sulfuric acid were used as received.

2.2. Preparation of films

Polypyrrole (PPy) containing different dopant ions was synthesized electrochemically by anodic oxidation of pyrrole in the presence of different electrolytes. Pyrrole

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PII S0032-3861(98)00319-X

Table 1
Properties of PPy films with different dopant ions

Film	Doping ratio[a]	σ (S cm^{-1})[b]	d[c] (g cm^{-3})[c]
PPy/BF_4	0.35	92	1.452
PPy/ClO_4	0.39	94	1.512
PPy/TsO	0.41	69	1.377
PPy/DBS	0.45	10	1.213

[a] Elemental analysis.
[b] Four-probe method.
[c] Flotation method.

monomer and electrolyte were dissolved in propylene carbonate containing 1% v/v water in concentrations of 0.06 and 0.05 mol L^{-1}, respectively. A constant current (0.125 mA cm^{-2}) was applied through a platinum plate (50 mm long, 20 mm wide, 0.1 mm thick) as anode and aluminium foil of 10 times the area as cathode with a potentiostat (HA-301, Hokutodenko Co. Ltd.). Polymerization was carried out at −20°C for 15 h. After polymerization, the PPy films were peeled from the platinum electrode, soaked in a large amount of propylene carbonate, and then dried overnight in a vacuum. The PPy films had a thickness of about 30 μm. The cross-linked poly(acrylic acid) (PAA) film was synthesized by esterification of PAA in the presence of a small amount of glycerin as a cross-linking reagent. PAA (0.69 mol L^{-1}) and glycerin (0.07 mol L^{-1}) were dissolved in 0.1 N aqueous H_2SO_4 and cast on the glass plate. The esterification was carried out for 12 h at 100°C in a drying oven. The PAA cast film was washed in a large amount of pure water to remove impurities and unreacted chemical reagent, and then dried in a vacuum. The PAA film obtained was transparent and flexible with a thickness of about 30 μm. The properties of the films produced are listed in Table 1.

2.3. Measurements

The doping ratio of each PPy was estimated from elemental analysis with an EA1108 (Carlo Erba Instruments Co. Ltd.). The electrical conductivity at 25°C was measured by a normal four-probe method with a digital multimeter (VOAC-7512, Iwatsu Co. Ltd.). The four copper wires were attached onto the gold plates (0.1 mm thick, 1 mm wide) evaporated on the PPy film (16 mm long, 2 mm wide, and 30 μm thick) with silver paste. The relative water vapour pressure (p/p_0) was measured with a hygrometer (MC-P, Panametrics Co. Ltd.).

The isothermal sorption curves were measured by the use of a quartz crystal microbalance (QCM) [15]. The PPy was polymerized on a gold electrode of the AT-cut QCM for 30 min, while the PAA was cast on the gold electrode under the same conditions described above. The thickness of PPy and PAA calculated from the density was about 1 μm. The frequency change was monitored with an universal counter (SC-7202, Iwatsu Co. Ltd.) and the sorption amount Δm (μg cm^{-2}) was given by

$$\Delta m = -\frac{10^{-6} \times \Delta F}{2.26 \times \Delta F_0^2} \quad (1)$$

where ΔF was the resonance frequency change (Hz), and F_0 the fundamental frequency of the QCM (9 MHz). The degree of sorption C (g g^{-1}) was defined as a weight ratio between Δm and dry polymer.

$$C = \frac{\Delta m(\mu\text{g cm}^{-2})}{\text{dry polymer}(\mu\text{g cm}^{-2})} \quad (2)$$

The measurements were carried out by reducing the relative water vapour pressure (p/p_0) at a rate of about 0.01 min^{-1}. If p/p_0 was held constant, no notable time variation of C was observed, indicative that the desorption of water was almost equilibrated.

Differential scanning calorimetry (d.s.c.) measurements of water in the PPy films were evaluated with a differential scanning calorimeter (d.s.c. 3100S, MAC Science Co. Ltd.) connected to a cooling unit. About 10 mg of dry films weighed in aluminium pans were hydrated by addition of pure water and then the pans were sealed hermetically. After the samples had been equilibrated at room temperature for 1 h, the d.s.c. measurements were carried out at heating rate of 10° min^{-1}. The pans were dried overnight in a vacuum after the d.s.c. scans and the accurate weight of the dry polymer was calculated. Prior to the measurement, the calibration was performed with distilled water standards.

3. Results and discussion

3.1. Sorption isotherms

In many cases, the sorption of gas molecules to various polymers can be described using a dual-mode sorption model in which the sorption is assumed to take place by two mechanisms: one is an ordinary dissolution described by a Henry's law type sorption and another is hole-fitting described by a Langmuir type sorption [16]. Thus the total degree of sorption C (g g^{-1}) defined as the weight ratio between water sorbed and dry polymer is expressed by

$$C = C_D + C_H = k_D p + \frac{C_H' bp}{1 + bp} \quad (3)$$

where C_D and C_H are degrees of sorption by Henry's law type sorption and Langmuir type sorption, respectively. k_D is the Henry's law solubility constant, p is the water vapour pressure, and C_H' and b are respectively the capacity constant and affinity constant for Langmuir type sorption.

Fig. 1 shows the isothermal sorption curves at 25°C for various PPys (thick line) and theoretical curves (thin line) where the C decreases monotonically with decreasing relative water vapour pressure p/p_0. The profiles are reproducible, so sorption of water to PPy is considered to be reversible. Wynne et al. [17] demonstrated that electrochemically

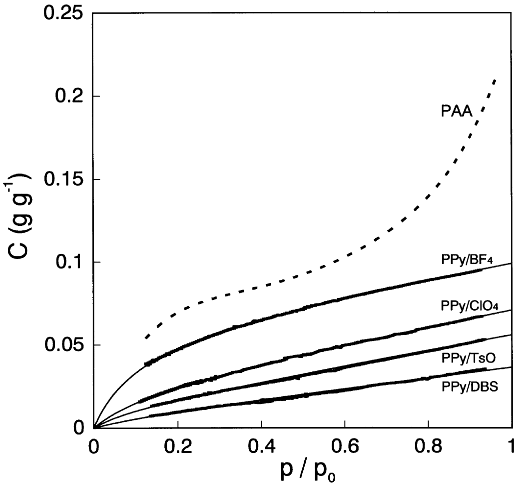

Fig. 1. Isothermal sorption curves of water vapour to PPy (solid line) and PAA (broken line) at 25°C measured by QCM technique. The theoretical curves for PPy are shown by the thin line.

synthesized polypyrrole films containing tosylate quickly took up about 3% water and the degree of sorption reached about 5% on exposure to ambient air for 3 months. They found that the sorption process was completely reversible, the entire weight of the sorbed water was lost on heating in vacuum at 105°C for 23 h.

The theoretical calculation for fitting the experimental data is carried out using the method of least squares, and the dual-mode sorption parameters obtained for various PPys are summarized in Table 2. One can see that the C_H', representing the maximum degree of sorption for the hole-fitting mechanism, increases in the order PPy/DBS < PPy/TsO < PPy/ClO$_4$ < PPy/BF$_4$. On the other hand, no notable tendency is observed for the Langmuir affinity constant b. This demonstrates that the number of sorbable Langmuir site increases in this order. Since the hydrophilicity of the dopant ion increases by the same amount as C_H', the hydration of dopant ions can occur in the Langmuir type sorption. The k_D appears to be independent of the kind of dopant ion, implying that hydration of PPy chains occurs at higher p/p_0. It is worth noting that the dual-mode sorption model holds over the whole experimental p/p_0 range from 0.1 to 0.95 even though the model can usually be applied only at low p/p_0 [18] because the degree of sorption increases abruptly at higher p/p_0 as can be seen for PAA (Fig. 1, broken line). This is well characterized by the Flory–Huggins sorption mechanism [19] where the interaction between water molecules is favoured over water–polymer interaction.

Table 2
Dual-mode sorption parameters for various PPys at 25°C

Film	k_D (g g^{-1} atm^{-1})	C_H' (10^{-2} g g^{-1})	b (atm^{-1})
PPy/BF$_4$	1.43	6.07	283
PPy/ClO$_4$	1.58	2.47	211
PPY/TsO	1.49	1.03	340
PPy/DBS	1.00	0.61	210

3.2. Cluster function

From Zimm–Lundberg theory [20], the clustering tendency of water in polymers is generally characterized by the cluster function as follows:

$$\frac{G_{11}}{V_1} = -\nu_2 \left[\frac{\partial(a_1/\nu_1)}{\partial a_1} \right]_{p,T} - 1 \tag{4}$$

where ν_1 and ν_2 are the volume fractions of water and polymer, respectively. V_1 is the molecular volume of water and G_{11} is the cluster integral. a_1 is the activity of water vapour which corresponds to the relative water vapour pressure p/p_0. Clustering is indicated when the cluster function (G_{11}/V_1) is greater than -1; the results are shown in Fig. 2. It can be seen that the G_{11}/V_1 of all PPys are smaller than -1 over the whole experimental p/p_0 range, indicating that the water molecules sorbed in the PPy are prevented from clustering. A decrease of G_{11}/V_1 at lower p/p_0 demonstrates that the interaction between water and polymer is more predominant than that between water molecules in the initial sorption process. Thus the drop of the G_{11}/V_1 for the PPy/TsO or PPy/DBS at lower p/p_0 can be explained in terms of the hydrophobic hydration of dopant molecules. In contrast, the PAA shows apparent clustering behaviour at higher p/p_0 because the G_{11}/V_1 value exceeds -1, indicating a formation of water clusters in the PAA film. The water in the PAA may bind tightly to the carboxyl groups along polymeric chains at low p/p_0, and then aggregate to form clusters at high p/p_0. This can be explained by additional sorption or condensation of water would take place on the already bound water where the interaction between water

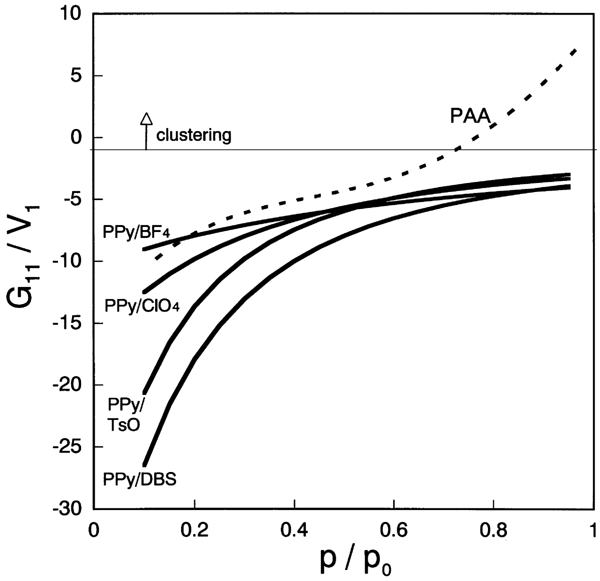

Fig. 2. Cluster function of water in various PPys (solid line) and PAA (broken line).

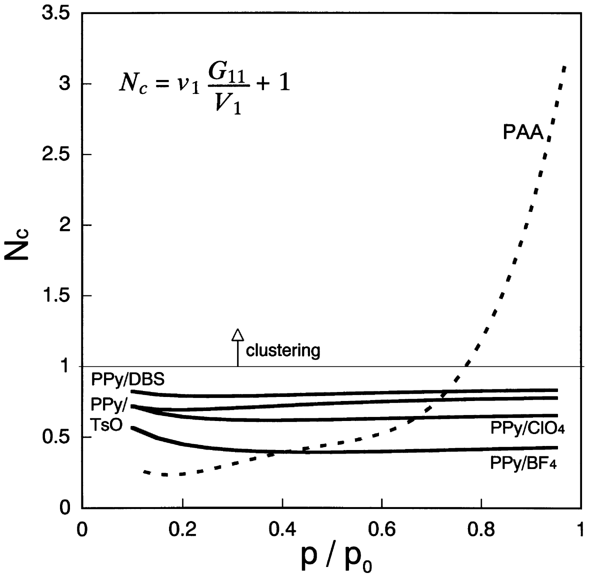

Fig. 3. Average cluster size of water in various PPys (solid line) and PAA (broken line).

molecules is favoured than water–polymer interaction characterized by the Flory–Huggins sorption mechanism [19].

The average cluster size N_c was calculated using the cluster function as follows [20]

$$N_c = \nu_1 \frac{G_{11}}{V_1} + 1 \quad (5)$$

In the present system, the N_c represents the average number of water molecules above that which is expected from the average concentration of the water in the polymer. Here, the N_c is not the real size of the clusters at the molecular level, but one of the indices describing the trend of clustering. The calculation result is shown in Fig. 3. One can see that the N_c values of all PPys are less dependent on p/p_0 and smaller than 1 over the whole p/p_0 range, indicating that the water molecules sorbed in the PPy are inhibited from clustering. On the other hand, the N_c of PAA abruptly rises at p/p_0 higher than 0.7 and attains a value of about 3. This demonstrates that a few water molecules aggregate to form a cluster in the PAA film. Similar clustering behaviour is observed for other hydrophilic polymers such as nylon-6 [21], cellulose [22], poly(2-hydroxyethyl methacrylate) [23], and poly(ethylene-co-methacrylic acid) ionomer [24]. Kusanagi et al. [25] studied water structures in various polymers using *FT*i.r. spectroscopy. They found that the i.r. spectra of water sorbed in the polymers showed two clearly distinct states: one was near the isolated state in hydrophobic polymers and the other was a clustered state in hydrophilic polymers. Thus, the sorption behaviour of PPy is rather similar to that of the hydrophobic polymers. This may be associated with a nature of the conductive polymers having a π-conjugated system. The delocalization of carbonium charges [26] would lower the ionic polarity and hydrophilicity of the polymeric chains, which may prevent the sorbed water molecules from clustering. On the other hand, the degree of sorption for PPy is about two orders of magnitude larger compared with hydrophobic polymers such as polyolefins at higher water vapour pressure. Thus, the PPy seems to be intermediate between polyelectrolyte and hydrophobic polymer. This feature of the PPy would be responsible for the quick and reversible bending and recovery motion of films [10,11,13] owing to the reversible sorption and desorption of water without clustering or successive condensation.

3.3. Physical state of water

The physical states of water in the PPy and PAA films are evaluated by d.s.c. measurement. The d.s.c. thermograms of water in various PPy films containing different water contents are shown in Fig. 4. The thermogram shows one endothermic peak in the heating trace which is attributed to the melting of freezable water in the film. A decrease of water content results in a shift of the melting peak to lower temperature and the peak becomes smaller and broader. Assuming that the heat of fusion for the water–ice transition ($\Delta H_0 = 79.7$ cal g^{-1}) is identical for each state of freezable water in the film [27], one can calculate the weight fraction of freezable water C_f (g g^{-1}) as follows

$$C_f = \frac{\Delta H_f \times m_w}{\Delta H_0 \times m_p} \quad (6)$$

where ΔH_f is the heat of fusion of freezable water in the melting trace. m_w and m_p are respectively the weight of total water and dry polymer. It is seen from Fig. 5 that the C_f decreases linearly with decreasing C. An extrapolation of C_f to zero leads to a critical water content C_0, representing a maximum content of freezable water, and the values are listed in Table 3. Below C_0, the freezable water disappears and water in the PPy behaves as a non-freezing bound water. Indeed, the d.s.c. thermogram showed no endothermic peak for the melting of water below C_0 over the whole experimental temperature range. It should be noted here that the C values in the isothermal sorption curves (Fig. 1) are smaller than C_0 for each PPy over the whole experimental p/p_0 range. This fact demonstrates that the water sorbed in the PPy behaves as a non-freezing bound water where the water molecules are directly bound to the PPy chains having no structural order to cause a water–ice transition. On the other hand, water in the PAA forms clusters and behaves in part as freezable water at p/p_0 higher than 0.87 where $C > C_0$.

The presence of a maximum content of non-freezing water indicates a finite number of available sites to which the water can bind. The maximum amount of bound water per repeated unit N_0 can be estimated as follows

$$N_0 = \frac{C_0([Py] + [dopant]x)}{M_{water}} \quad (7)$$

where [*Py*] and [*dopant*] are molecular weights of pyrrole unit and dopant ion, respectively. x is the doping ratio and

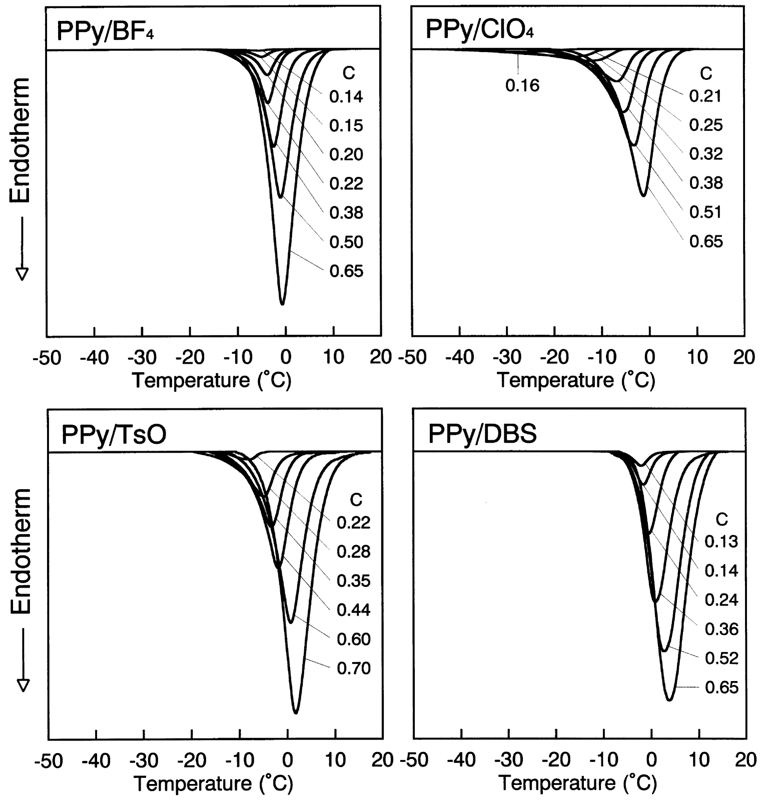

Fig. 4. d.s.c. heating thermograms of various PPy films with different water content. Heating rate: 10° min^{-1}.

Table 3
The maximum amount of non-freezing water (C_0) and maximum amount of non-freezing water per monomeric unit (N_0) for various polymers

Film	C_0 (g g^{-1})	N_0
PPy/BF_4	0.14	0.76
PPy/ClO_4	0.13	0.76
PPy/TsO	0.21	1.60
PPy/DBS	0.11	1.33
PAA	0.17	0.67

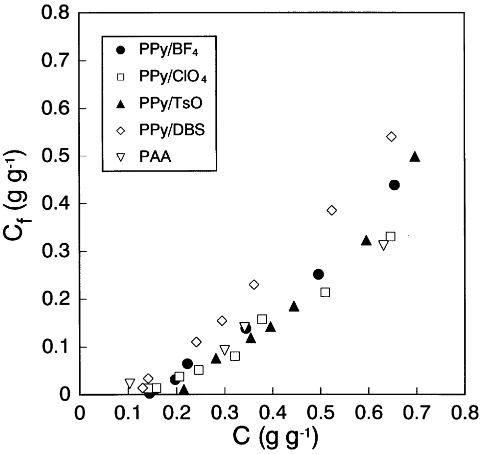

Fig. 5. The relation between the fraction of freezable water (C_f) and total water content for films. PPy/BF_4 (●), PPy/ClO_4 (□). PPy/TsO (▲), PPy/DBS (◇), and PAA (▽).

M_{water} is the molecular weight of water. From Table 3, the N_0 values of PPy/BF_4 and PPy/ClO_4 are 0.76, which implies that when the amount of bound water is greater than 0.76 per pyrrole unit, the freezable water appears in the d.s.c. thermogram. On the other hand, the N_0 values of PPy/TsO and PPy/DBS are relatively larger, which may be due to the hydrophobic hydration of dopant ions.

4. Conclusions

The isothermal sorption curves for the PPy containing various dopant ions can be described by the dual-mode sorption model over the whole experimental p/p_0 range from 0.1 to 0.95. The $C_H{}'$ increases in the order PPy/DBS $<$ PPy/TsO $<$ PPy/ClO_4 $<$ PPy/BF_4, while b and k_D appear to be independent on the kind of dopant ion. Cluster function d.s.c. measurements indicate that the water sorbed in the PPy behaves as non-freezing bound water which is rather isolated and prevented from clustering over the whole experimental p/p_0 range.

References

[1] Winokur MJ, Wamsley P, Moulton J, Smith P, Heeger AJ. Macromolecules 1991;24:3812.
[2] Herod TE, Schlenoff JB. Chem Mater 1993;5:951.
[3] Otero TF, Rodriguez J. In: Aldissi M, editor. Intrinsically conducting

polymers, an emerging technology. Dordrecht: Kluwer Academic Pub. 1993:179.

[4] Chen X, Inganäs O. Synthetic Metals 1995;74:159.

[5] Baughman RH, Shacklette LW, Elsenbaumer RL, Plichta EJ, Becht C. In: Lazarev PI, editor. Molecular electronics. Dordrecht: Kluwer Academic Pub. 1991:267.

[6] Pei Q, Inganäs O. J Phys Chem 1992;96:10507.

[7] Pei Q, Inganäs O. Synthetic Metals 1993;55-57:3718.

[8] Kaneto K. Kobunshi 1994;43:856.

[9] Smela E, Inganäs O, Lundström I. Science 1995;268:1735.

[10] Okuzaki H, Kunugi T. J Polym Sci Polym Phys 1996;34:1747.

[11] Okuzaki H, Kunugi T. J Appl Polym Sci 1997;64:383.

[12] Okuzaki H, Kuwabara T, Kondo T, Kunugi T. J Polym Sci Polym Phys 1998, in press.

[13] Okuzaki H, Kuwabara T, Kunugi T. Polym Commun 1997;38:5491.

[14] Okuzaki H, Kunugi T. J Polym Sci Polym Phys Rapid Commun 1998;36:1591.

[15] Thomas JH, Sharma SP. J Vac Sci Tech 1976;13:549.

[16] Barrer RM, Barrie JA, Slater J. J Polym Sci 1985;27:177.

[17] Wynne KJ, Street GB. Macromolecules 1985;18:2361.

[18] Stannett VT, Koros WJ, Paul DR, Lonsdale HK, Baker RW. Adv Polym Sci 1979;32:69.

[19] Flory PJ. Principles of polymer chemistry. Ithaca, NY: Cornell University Press, 1953.

[20] Zimm BH, Lundberg JL. J Phys Chem 1956;60:425.

[21] Frank B, Frübing P, Pissis P. J Polym Sci Polym Phys 1996;34:1853.

[22] Starkweather HW Jr.. Macromolecules 1975;8:476.

[23] Sun Y-M, Lee H-L. Polymer 1996;37:3915.

[24] Itoh K, Tsujita Y, Takizawa A, Kinoshita T. J Appl Polym Sci 1986;32:3335.

[25] Kusanagi H, Yukawa S. Polymer 1994;35:5637.

[26] Brédas JL, Scott JC, Yalushi K, Street GB. Phys Rev 1984;B30:1023.

[27] Itoh K, Tsujita Y, Takizawa A, Kinoshita T. J Appl Polym Sci 1986;32:3335.