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Morphology and electrical properties of polyacetylene–polyisoprene conducting copolymers

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The solid state structure of soluble conducting diblock copolymers of polyacetylene–polyisoprene (PA-PI), before and after I_2-doping, was investigated in this study using scanning electron microscope (SEM) and small angle X-ray scattering (SAXS). The SAXS study demonstrated that I_2-doping of the PA-PI diblock copolymer in the solid state resulted in the formation of a rod-like structure of polyacetylene chains, at the nanometre scale, caused by the strong self-association of the doped polyacetylene segments. On the other hand, the SEM micrographs revealed a doping-induced morphology transformation from a homogeneous state to a phase-separated fibrous network at the micrometre scale reflecting the formation of a pseudo interpenetrating polymer network (PIPN) due to the thermodynamic immiscibility between the I_2-doped polyacetylene 'rods' and polyisoprene chains. These results indicate that multiphase materials with ordered structures ranging from the nanometre to micrometre scale can be obtained by I_2-doping of the PA-PI diblock copolymers in the solid state. The PIPN network thus formed plays an important role in regulating the electrical properties of the I_2-doped copolymer films. © 1997 Elsevier Science Ltd. All rights reserved.

(Keywords: conducting copolymer; phase separation; morphology and electrical properties)

INTRODUCTION

Owing to its simple conjugated molecular structure and fascinating electronic and photonic properties, polyacetylene (PA) has been and is still being most widely studied as a prototype for other conjugated polymers[1]. The intractability (insoluble, infusible and unmeltable) of polyacetylene, however, precludes not only its application but also characterization at the molecular level. It now appears that polyacetylene may be solubilized by making copolymers with polyisoprene, polystyrene or polybutadiene[2]. Two different synthetic routes for producing soluble diblock copolymers of polyacetylene and polyisoprene (PA-PI) have been reported[3–5]. Both involve anionic polymerization of isoprene by *n*-BuLi to generate polyisoprenyllithium chains and subsequent Ziegler–Natta copolymerization of acetylene onto the living polyisoprene chains. But, they differ from each other by using either $Ti(OBu)_4$ or $CoCl_2$ as a constituent of the Ziegler–Natta catalysts, and the resultant materials are reported to be quite different[6]. For instance, polyacetylene chains in the PA-PI copolymers synthesized using the titanium catalyst exist largely in the *trans* form whereas the material produced from the cobalt catalyst contains mostly *cis*-polyacetylene. Of them, the PA-PI copolymers produced by the cobalt catalyst seems to be less discussed in the literature[7]. In particular, as far as we are aware, no detailed study of their morphology or electrical properties in the solid state has been reported[7].

The PA-PI diblock copolymers prepared by the anionic to Ziegler–Natta route present an unusual situation where the stiffness characteristic of insoluble conjugated polyacetylene chains and the high flexibility and solubility associated with polyisoprene chains are combined into one macromolecule forming a rod–coil type diblock copolymer. Rod–coil block copolymers have recently attracted considerable attention[8,9]. Due to the extreme contrariety in physical properties between these two blocks, the copolymers of PA-PI may be expected to show phase separation in solution and domain structure in the solid state. In our previous publication[10], it has been demonstrated that PA-PI copolymers prepared by the cobalt catalyst form worm-like micelles in solution by ageing, and that I_2-doping of the PA-PI copolymer solution induces a phase transformation from the worm-like micelle to a lamellar structure.

A well established fibrillar morphology in polyacetylene homopolymer has been recognized to play an important role in the doping process and charge transportation[11–13]. Consequently, a number of ingenious synthetic methods leading to polyacetylene homopolymers with distinct morphologies, and hence electrical properties, have been reported[14]. For example, by ageing Shirakawa's catalyst[11] in silicone oil at 150°C, Naarmann and Theophilou[15,16] have successfully prepared ordered polyacetylene of extremely high conductivity ($10^5 \Omega^{-1}$ cm^{-1} after I_2-doping). In our recent investigation on the consequences of the micellization

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and doping on morphologic structures of the PA-PI diblock copolymers in the solid state, we found that I_2-doping of the PA-PI copolymer films leads to the formation of a pseudo interpenetrating polymer network (PIPN) arising from the strong self-association of polyacetylene segments coupled with the thermodynamic immiscibility between polyisoprene and the I_2-doped polyacetylene chains.

Generally speaking, an interpenetrating polymer network (IPN) refers to two or more distinctly crosslinked polymers mutually held together in a network form predominantly by chain–chain entanglement, rather than by covalent bonds between them. In such systems, if only one of the polymers is crosslinked, a pseudo-IPN (PIPN) or semi-IPN is formed. On the other hand, if the chemical crosslinks are replaced by physical crosslinks (e.g. the crystallites in semicrystalline polymers, the ionic portions of ionomers, etc.) the so-called 'thermoplastic IPN or thermoplastic PIPN' results (see ref. 17 for example). The properties, such as mechanical, thermal and electrical properties, of the individual consisting polymers may be significantly altered by IPN or PIPN formation, which often leads to materials of superior properties. Very recently, some pseudo or full conducting IPNs have been synthesized by chemically crosslinking one or more of the consisting polymers, of which at least one of the components is an electrically conducting polymer[18–21]. The materials thus prepared were reported to exhibit novel electrical properties with a very low percolation threshold and considerably enhanced conductivity stability[18,19]. However, the formation of conducting thermoplastic IPN or thermoplastic PIPN by physical crosslinking has yet been recognized. In this paper, we report scanning electron microscopic (SEM) and small-angle X-ray scattering (SAXS) study on the first formation of conducting thermoplastic PIPN induced by I_2-doping of the PA-PI diblock copolymers in the solid state. The implications of this to the electrical properties of the copolymer films are also discussed.

EXPERIMENTAL

Materials

PA-PI block copolymers consisting mainly of *cis*-polyacetylene blocks in the macromolecules were freshly synthesized at −78°C by the cobalt catalyst method, and used as starting materials. The synthesis and characterization of these copolymers have been previously described[5,6,10]. Most preparations were performed in toluene so 1,4-polyisoprene was the dominant component[10]. For convenience, we designate subsequently the diblock copolymers of polyacetylene and polyisoprene used in this study as PA_N-PI_M, where N and M are molecular weights of polyacetylene and polyisoprene blocks, respectively.

Doping

Prior to I_2-doping, all of the sample films were dried under a dynamic vacuum ($<10^{-5}\tau$) until a constant weight was recorded for a reference film, which had been pumped under the same conditions. Doping was then achieved by exposing the dry samples to iodine vapour in an air-tight container at room temperature. The extent of doping was controlled primarily by the reaction time with iodine, and the iodine levels were determined, at intervals, by the increase in weight of the reference film, which had been thoroughly pumped to take off any excess iodine immediately before weighing.

Characterization

For SEM observations and conductivity measurements, the copolymer films were prepared by spin-casting of the as-synthesized PA-PI solution onto microscope cover slips followed by drying under the dynamic vacuum ($<10^{-5}\tau$). The conductivity measurements were made using the standard van der Pauwe DC four-probe method with a measuring chamber sealed under vacuum[22], while the SEM micrographs were taken on a Stereoscan 360 microscope after coating the sample films with a homogeneous gold layer of *ca* 50 Å by sputtering. In the case of ultraviolet/visible/near infrared (u.v./vis./n.i.r.) measurements, thin films were cast directly onto the inner surface of a 1 mm quartz cell and the absorption spectra measured *in situ* (under vacuum) on a Lambda 9 u.v./vis./n.i.r. spectrometer. The SAXS scattering measurements were performed on free-standing copolymer films using a Huxley–Holmes camera, which had been described in detail elsewhere[6,10,23,24]. Briefly, copper K_α radiation with $\lambda = 1.54$ Å was used and the SAXS data were presented as absolute intensity, $I(Q)$, vs the momentum transfer, $Q = (4\pi/\lambda)\sin\theta$, where θ is half the scattering angle. X-ray exposure was kept to a minimum by using a one-dimensional position sensitive detector, with which the whole scattering pattern could be recorded simultaneously[24]. The scattering intensity was corrected for electronic background and converted into an absolute scale using the scattering from 1 mm water for calibration[10,24,25]. The data were further corrected for smearing effects due to the slit collimation according to the 'deconvolution' procedure of Lake[6,10,26]. All the measurements were carried out at room temperature (25°C) unless otherwise stated.

RESULTS AND DISCUSSION

I_2-doping

U.v./vis./n.i.r. spectra. We have previously investigated the I_2-doping process of PA-PI copolymer films using spectroscopic techniques including u.v/vis./n.i.r.

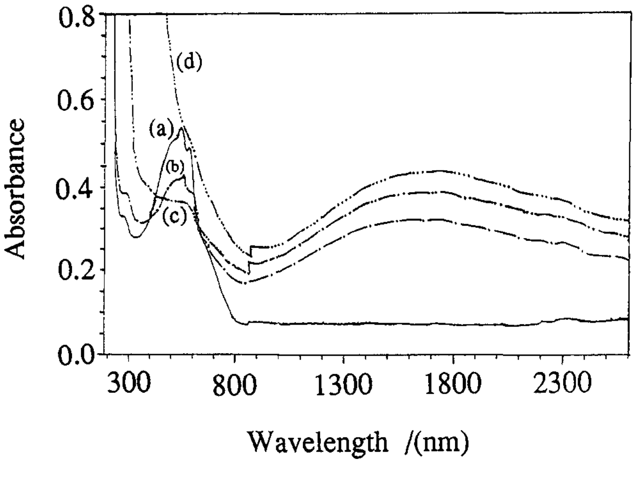

Figure 1 U.v./vis./n.i.r. spectra of the PA_{753}-PI_{8000} film before and after I_2-doping. I_2-doping time: (a) 0 h; (b) 2 h; (c) 10 h; (d) 72 h

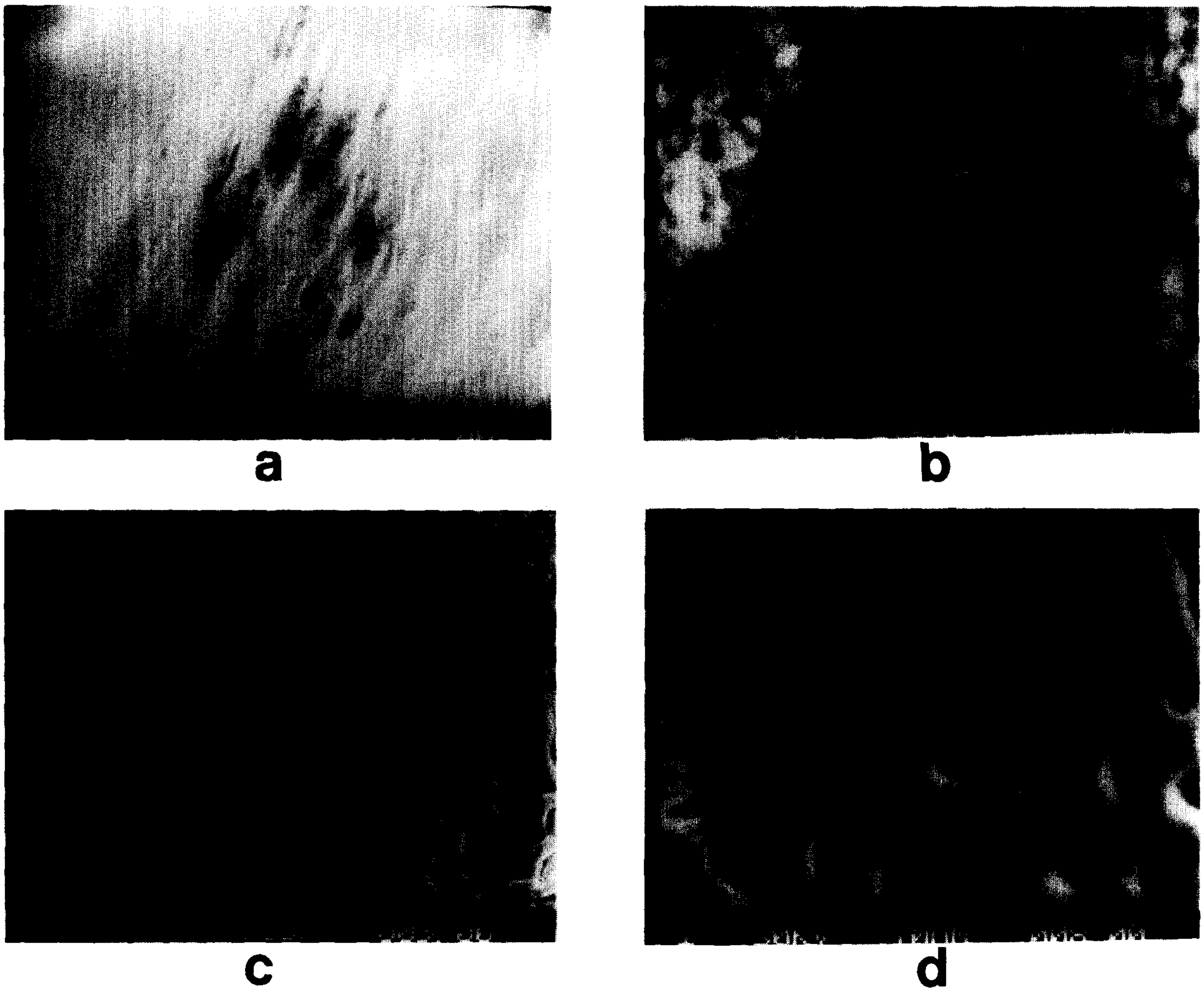

Figure 2 SEMs of the PA_{753}-PI_{8000} film before and after I_2-doping. I_2-doping time: (a) 0 h; (b) 0.2 h; (c) 2 h; (d) as for (c), under a higher magnification

and Fourier transform infra-red (*FT*i.r.)[27]. The main results are reviewed here aiming at providing some necessary guidelines for this study. Upon doping the PA-PI copolymer films with iodine, an immediate colour change from purple to lustrous blue was observed, presumably indicating that *cis*-polyacetylene chains in the copolymer macromolecules had been rapidly converted into the *trans*-isomer, as is the case with I_2-doping of *cis*-polyacetylene homopolymer[1]. As the doping proceeded further, the intense blue colour turned into a silvery brassy sheen. *Figure 1* shows the u.v./vis./n.i.r. spectra recorded at various stages of the I_2-doping reaction for a PA_{753}-PI_{8000} copolymer film. As expected, *Figure 1a* exhibited two vibronic peaks at 548 and 583 nm characteristic of *cis*-polyacetylene chains[1] in the pristine PA-PI film. As the doping proceeded, however, a broad band developed in the n.i.r. region (*ca* 1800 nm) and the polyacetylene bands in the visible region became obscured (*Figure 1b*). Further doping caused the absorption bands corresponding to the interband transition to disappear in the visible region, while the broad band observed at the near i.r. region became more intense (*Figure 1c*). After extensive reaction with iodine, however, there was a great increase in optical intensity below 800 nm (*Figure 1d*) reflecting the occurrence of the I_2-induced conjugation of 1,4-polyisoprene chains in the copolymer macromolecules. 1,4-Polyisoprene is known to react with iodine producing conjugated segments[28-31]. The broad band centred on *ca* 1800 nm was assigned to a transition from the valence band to a hole level associated with the I_2-doped polyacetylene[1,32]. This assignment is, at least partially, supported by the appearance of the isosbestic point at about 600 nm on the u.v./vis./n.i.r. spectra in *Figures 1a–1c* indicating that there was an interconversion between the absorbing species corresponding to the 548/583 nm absorption peaks and those represented by the 1800 nm band.

The above optical spectroscopic measurements, together with our *FT*i.r. results previously reported[27], indicate that with proper control of the doping time (say $\leq$20 h) I_2 can selectively act as a dopant for polyacetylene chains in the PA-PI diblock copolymer macromolecules. Although this is consistent with an induction time of about 20 h required for the formation of conjugated sequences in 'I_2-doped' polyisoprene homopolymer films[28], it cannot be ruled out that a substantial amount of I_2 may have added into the 1,4-polyisoprene backbone prior to the HI elimination[28-31]. In view of these findings, the doping levels for all of the following experiments were controlled to be below the onset for I_2-induced conjugation of polyisoprene in order to avoid unnecessary confusion and focus our attention on the I_2-doping of polyacetylene chains in the copolymer films.

Morphology

Electron microscopic studies. We have performed a systematic SEM study on the effect of doping on morphology of the PA-PI diblock copolymer films. For a freshly synthesized and freshly cast PA-PI diblock copolymer film, as shown in *Figure 2a*, an almost featureless surface was observed. This could indicate that the electron contrast between distinct domains, if any, in the undoped copolymer film is not sufficient for them to be visualized without staining. But, our SAXS results (*vide infra*) suggest that polyisoprene and polyacetylene chains in the freshly prepared copolymer film mix homogeneously at the molecular level leading to a disordered state, although ageing has been demonstrated to cause a slow aggregation of the PA-PI copolymer chains in solution[10]. Upon doping (*Figure 2b*), however, dispersed worm-like micelles developed due to the doping-induced aggregation of polyacetylene chains[10]. As the doping proceeded further, the static electrical interactions between the doped polyacetylene chains and their counterions brought the neighbouring micelle cores together to form a thermoplastic PIPN network structure, as shown in *Figure 2c*. Similar SEM micrographs to *Figure 2c* have been reported for some PIPN and IPN systems[33,34]. Closer inspection of *Figure 2c* under a higher magnification (*Figure 2d*) clearly shows the interpenetrating network structure.

We note, however, that polyacetylene–polystyrene diblock copolymers prepared by the titanium catalyst[35] or polyacetylene–polyisoprene copolymers synthesized in tetrahydrofuran (THF) by the cobalt catalyst[36] forms, upon I_2-doping, a spheric morphology with polyacetylene particles dispersed in the polystyrene or polyisoprene matrix. For materials prepared in THF, 3,4-addition has been shown to be the dominant process for producing polyisoprene blocks in the PA-PI copolymer chains[36], and 3,4-polyisoprene, unlike 1,4-polyisoprene, is not susceptible to the iodine-addition[28–31]. Thus, the chemical nature of the non-conducting blocks can also have far-reaching consequences on the morphology of the conducting copolymer films. The spheric morphology accounts well for the low conductivity and high percolation threshold observed in these materials (*vide infra*)[35].

SAXS studies. As seen above, the SEM examinations clearly indicate a phase separation induced by I_2-doping of the PA-PI diblock copolymers in the solid state. In order to investigate the phase separation behaviour at the molecular level, we carried out the SAXS measurements. Due to the relatively high value of the scattering length density and strong tendency for aggregation associated with polyacetylene chains, the scattering function from the PA-PI has previously been demonstrated to reflect more strongly the polyacetylene structure in the diblock copolymer samples[10].

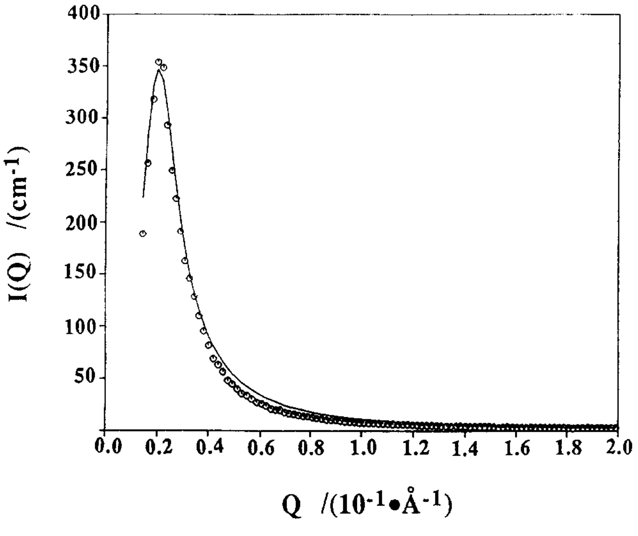

Figure 3 SAXS curve for the pristine PA_{753}-PI_{8000} film. The solid line is a model fit-see text

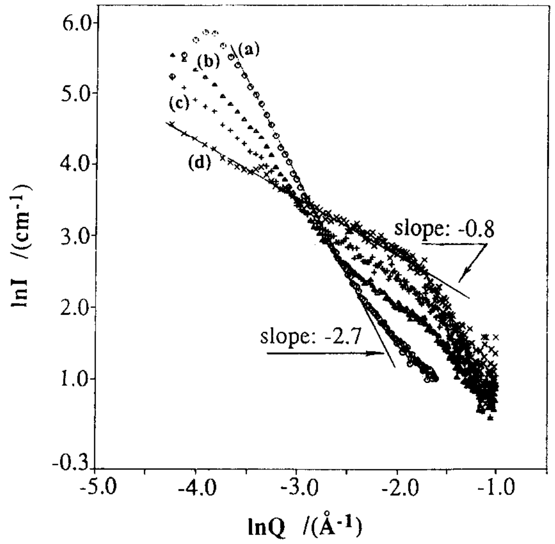

Figure 4 Ln I vs ln Q plots for the PA_{753}-PI_{8000} film at various stages of I_2-doping. (a) Before doping; (b) I_2 = 8.52 wt%; (c) I_2 = 13.81 wt%; (d) I_2 = 22.95 wt%. (The apparently high doping level based on the amount of polyacetylene[1] indicates the occurrence of iodine-addition into the 1,4-polyisoprene backbone–see text)

As shown in *Figure 3*, a broad peak at low-Q region (Q = 0.020 Å^{-1}) was observed with care for the freshly prepared and freshly cast PA_{753}-PI_{8000} copolymer film. The observed low-Q peak may well be attributed to a correlation hole effect arising from a homogeneous state in the as-cast copolymer film (see below)[37–43], as indicated by the SEM observation shown in *Figure 2a*. For I_2-doped PA-PI copolymer films, however, the strong aggregation behaviour of the I_2-doped polyacetylene blocks in the copolymer chains rapidly led to a domain structure, which obscured the low-Q peak (see *Figure 4*). The correlation hole effect was first introduced by de Gennes[37] to explain the scattering behaviour from partially deuterated polymers in melts. Particularly, in the case where every polymer chain contains a block of labelled (e.g. deuterium labelling) and a block of unlabelled segments, de Gennes demonstrated[37] that each segment is surrounded by a domain, inside of which the concentration of the like segments from other chains is reduced leading to a peak in neutron scattering by the partly deuterated chains at the low-Q region. This depletion of interchain segment–segment correlation is called the correlation hole. On the basis of the simple correlation hole argument, several theoretical approaches have been developed to account for the low-Q scattering peak from homogeneous diblock copolymers[42,43]. Most of them give the same structure factor.

By using the random phase approximation (RPA) theory[37], Leibler[44] and Bates[45] have deduced equation (1) as the homogeneous state structure factor for any combination of A–B diblock copolymer and A homopolymer, which can be applied to the very early stages of phase separation[46]

$$S^{-1}(Q) = F(N_{AB}, N_A, \Phi_{AB}, \Phi_A, f, a_A, a_B, Q) - 2\chi_{AB} \tag{1}$$

where N_i, Φ_i, and a_i are the weight-average degree of polymerization, volume fraction, and Gaussian coil statistical length for species i, respectively; f represents the composition of the diblock copolymer given by the ratio of the number of A monomer units to the total number of monomer units per copolymer chain, N_{AB}; χ_{AB} is the Flory–Huggins segmental interaction parameter; $\Phi_{AB} + \Phi_A = 1$ is a result of incompressible mixing; and F is given by the following equations:

$$F(N_{AB}, N_A, \Phi_{AB}, f, a_A, a_B, Q) = \frac{(N_A/N_{AB})(1-\Phi_{AB})g(R_A) + \Phi_{AB}g_1(1)}{N_A\Phi_{AB}(1-\Phi_{AB})g_1(f)g_1(1-f) + N_{AB}\Phi_{AB}^2G_{AB}} \tag{2}$$

where

$$g(x) = 2(x^2Q^2 + e^{-x^2Q^2} - 1)/x^4Q^4 \tag{3}$$

$$G_{AB} = g_1(f)g_1(1-f)^{-1/4}[g_1(1) - g_1(\mathrm{f}) - g_1(1-f)]^2 \tag{4}$$

$$g_1(f) = 2\left(fR_{AB}^2Q^2 + e^{-fR_{AB}^2Q^2} - 1\right)/R_{AB}^4Q^4 \tag{5}$$

$$R_{AB}^2 = (N_{AB}/6)[fa_A^2 + (1-f)a_B^2] \tag{6}$$

with R_{AB} corresponding to the overall radius of gyration of the diblock copolymer; and $R_A^2 = a_A^2N_A/6$ representing the radius of gyration of the homopolymer A.

On the other hand, according to the SAXS theory[47], the absolute scattering intensity, $I(Q)$, from a homogeneous (single phase or disordered) polymer system containing two different components is given by a product of the homogeneous state structure factor $S(Q)$ and a contrast factor:

$$I(Q) = V[(b_A/V_A) - (b_B/V_B)]^2S(Q) \tag{7}$$

where b_i and V_i are the scattering length and volume of a scattering unit for component i, respectively; and $V = \Phi_AV_A + \Phi_BV_B$ as a consequence of the above definitions for Φ_i and V_i. Therefore, the Flory–Huggins segmental interaction parameter χ_{AB} for a diblock copolymer in a homogeneous state could be conveniently obtained by fitting experimental small angle scattering data to equations (1)–(7).

We fitted the SAXS data in *Figure 3* with equations (1)–(7) by using a calculated value of 9.6 Å to be the Gaussian coil statistical length for polyisoprene (calculated from the radius of gyration of polyisoprene coils in θ-solvent[6,10,24] since polymer chains in the melt are ideal[37]) and the experimental values of the scattering length intensity 9.15×10^{10} and $10.90 \times 10^{10}\,\mathrm{cm}^{-2}$ for polyisoprene and polyacetylene, respectively[10]. The best fitting gives a value of 0.1110 for the χ_{AB} and a value of *ca* 40 Å as the statistical length for the polyacetylene chains in the copolymer. The $\chi_{AB} = 0.1110$ is slightly less than the critical Flory–Huggins segmental interaction parameter, $(\chi_{AB})_{cr} = 0.1112$ (see Appendix). This could explain not only the formation of a homogeneous state in the freshly prepared PA_{735}-PI_{8000} film but also the ease for aggregation upon I_2-doping or ageing. The value of *ca* 40 Å as the statistical length for the PA_{735} corresponds to its chain length suggesting that polyacetylene blocks in the PA-PI films are fairly stretched facilitating the formation of the PIPN network.

As seen in *Figure 4*, the low-Q peak corresponding to the correlation hole effect rapidly disappeared upon doping due to aggregation. This was accompanied by a monotonous change from *ca* −2.7 (*Figure 4a*) to *ca* −1.0 (*Figure 4d*) in the slope of the $\ln I$ vs $\ln Q$ plots over the low to medium range of Q. The value of *ca* −1.0 as the slope for the $\ln I$ vs $\ln Q$ plot indicates the formation of a rod-like structure, whereas the corresponding slopes for two-dimensional worm-like micelles have been known[10] to be between −2 and −2.5. Thus *Figure 4* suggests, once again, a phase transformation from the homogeneous state (*Figure 2a*), possibly through the worm-like micelles (*Figure 2b*), to a rod-like (network) structure (*Figure 2c*). The slope of the $\ln I$ vs $\ln Q$ plots (*Figure 4*) at high-Q region monotonously approached to *ca* −4 (i.e. Porod's slope) indicating that I_2-doping produced a sharp interface between the PA and PI phases[10,47].

The doping level dependence of the modified distance distribution function[10,47], $f(r) = P(r)/r$ (*Figure 5*) provides further insight about the phase transition induced by the I_2-doping. (Details about how the Fourier transformation was done to obtain the $f(r)$ function from the scattering curves of $I(Q)$ vs Q have been previously described[10].) As seen in *Figure 5*, the decreasing dimension of the cross-section from the worm-like micelles to a rod-like structure, during I_2-doping, is clearly illustrated by a shift of the maximum to smaller r values and the progressively decreasing in the slope of the linear descent at high r regions as well[47,48]. In fact, *Figure 5c* is nothing but a typical $f(r)$ function for elongated rod-like (network) structures[47,48]. In the light of the above results we propose some schematic ideas of

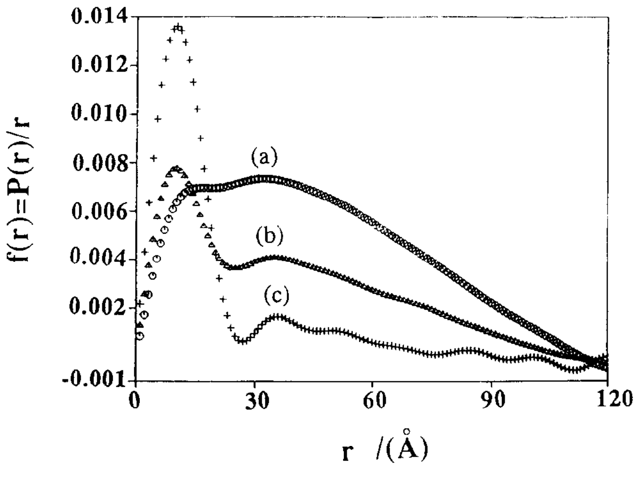

Figure 5 The modified distance distribution function for the I_2-doped PA_{753}-PI_{8000} film. (a) Before doping; (b) $I_2 = 8.52$ wt%; (c) $I_2 = 22.95$ wt%

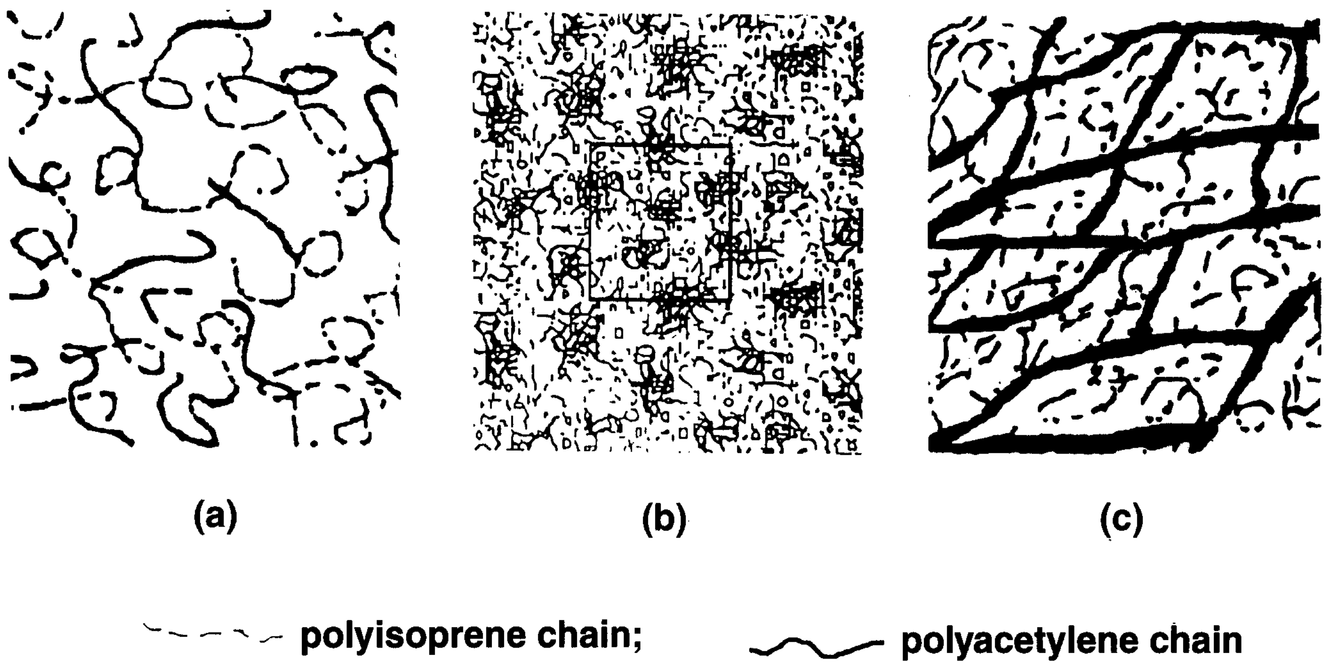

Figure 6 Schematic representation of the molecular organization in diblock copolymer films of polyacetylene and polyisoprene synthesized by the cobalt catalyst in toluene. (a) Before doping, homogeneous state; (b) low level I_2-doping, worm-like micelles (note that the selected area looks geometrically similar to the whole); (c) heavily doped by I_2, rod-like network

the doping-induced morphologic changes for the freshly prepared PA-PI copolymer films (*Figure 6*).

Electrical properties

General electrical behaviour. From foregoing discussions, it seems clear that I_2-doping of the PA-PI diblock copolymer in the solid state induces a phase transformation from the homogeneous state to a rod-like network, as schematically shown in *Figure 6*. In what follows, we undertake a brief demonstration of the consequences of the phase behaviour on electrical properties of the PA-PI diblock copolymer films.

Similar to I_2-doping of polyacetylene homopolymer[1], it was noted that the kinetics of I_2-doping of the PA-PI copolymer films was characterized by a monotonous increase in conductivity with doping time until a plateau region was reached. (Typically, the conductivity of a PA-PI copolymer film with polyacetylene content above the percolation threshold, *ca* 7 wt% of polyacetylene – see below – was found to increase by *ca* 10 order of magnitude, before levelling off, within the first 2 h of I_2-doping.) Unlike its homopolymer counterpart, however, conductivity measurements on I_2-doped PA-PI films with various different compositions show an apparent percolation threshold at about 7 wt% $(CH)_x$, i.e. the minimum polyacetylene content required for the PA-PI copolymer materials to be conducting after I_2-doping. This value of the percolation threshold for the PA-PI copolymers prepared by the cobalt catalyst in toluene seems unusually low, especially compared with the corresponding value of 16% v/v for polyacetylene-polystyrene copolymers produced from the titanium catalyst[35]. As mentioned above, however, a globular morphology has been reported for the latter (*vide supra*)[19,35].

In view of the great difference in morphology between these two copolymers, we believe that it is the rod-like network of the I_2-doped polyacetylene in the PA-PI copolymers prepared by the cobalt catalyst in toluene which greatly reduces the percolation threshold. This is because the percolation threshold for rod-like conducting particles in an insulating matrix is known to be much less than that for spherical conducting particles in the same insulating matrix[49]. In fact, the observed percolation threshold can be qualitatively explained in terms of the PIPN network formation as follows: For PA-PI samples with polyacetylene wt% less than 7%, the amount of polyacetylene chains in the material may not be enough to form a continuous network, after doping, so the conductive domains are insulated from each other by the polyisoprene medium. As a result, the electrically conducting behaviour could not be observed for these materials. For PA-PI copolymer films with higher polyacetylene contents, however, the I_2-doped polyacetylene chains appear to overlap leading to the formation of a rod-like network for transportation of electrons. Hence, a percolation threshold corresponding to the insulator-semiconductor transition was observed at the particular polyacetylene content of *ca* 7 wt%. Nevertheless, further increasing the polyacetylene percentages may only cause the volume of the conductive domains to be increased without any significant increase in the pathway for charge carriers due to the strong tendency for aggregation of the I_2-doped polyacetylene chains.

Conduction mechanism. The temperature dependence of conductivity for the PA-PI diblock copolymer films with different wt% contents of polyacetylene has been measured in this study in order to gain a further insight on the mechanism of conduction[1,50–52]. Typical results are shown in *Figure 7* as a function of reciprocal of the absolute temperature for sample films with polyacetylene content in the range between 8 and 14 wt%. In general, we found that the conductivity of the I_2-doped PA-PI copolymer films increased with increasing temperature

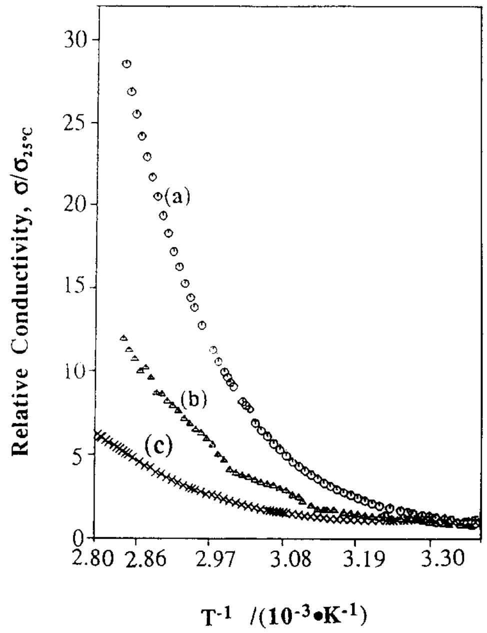

Figure 7 Typical plots of $\sigma/\sigma_{25^\circ C}$ vs $1/T$ for various I_2-doped PA-PI films. (a) PA = 8.65 wt%; (b) PA = 11.17 wt%; (c) PA = 13.85 wt%

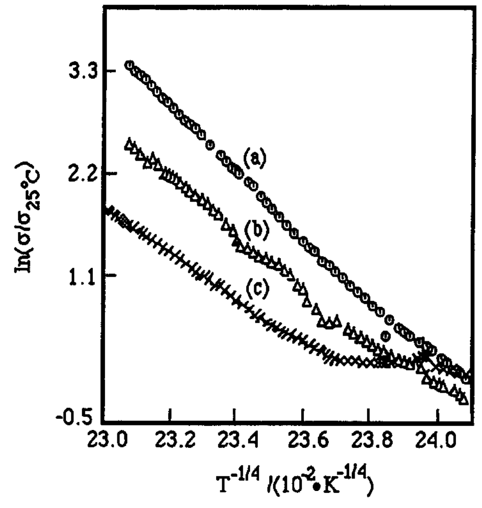

Figure 8 $\ln(\sigma/\sigma_{25^\circ C})$ vs $1/T^{1/4}$ for the I_2-doped PA-PI films (data from *Figure 7*). (a) PA = 8.6 wt%; (b) PA = 11.17 wt%; (c) PA = 13.85 wt%

reflecting a semiconductor-type behaviour, as is also the case for the I_2-doped polyacetylene homopolymer[1].

On the basis of a three-dimensional hopping model, Mott has deduced a formula for temperature dependence of conductivity in non-crystalline materials as follows[53]:

$$\sigma = A\exp(-B/T^{1/4}) \qquad (8)$$

where $B = 2(3/2\pi)^{1/4}[\alpha^3/kN(E_F)]^{1/4}$; k is the Boltzmann Constant; α^{-1} is the electronic state localization length; and $N(E_F)$ is the density of states at Fermi level.

Experimentally, many four-probe d.c.-conductivity measurements carried out on doped polyacetylene homopolymers have shown that the temperature dependence of the d.c.-conductivity obeys $\ln\sigma(T) \sim T^{-1/4}$, which is consistent with a charge transport process governed by the three-dimensional hopping mechanism[1,50,54]. In the present study, it may be difficult to extract the exact values for the physical parameters of α^{-1} and $N(E_F)$ from a numerical fitting of equation (8) to the experimental data, since both the α^{-1} and $N(E_F)$ are uncertain. However, some qualitative information on the conduction mechanism could be obtained by plotting $\ln\sigma$ against $T^{-1/4}$. As seen in *Figure 8*, for the PA-PI copolymer films, the logarithmic conductivity depends linearly on the $T^{-1/4}$, within experimental errors, indicating a three-dimensional hopping mechanism for the charge transportation. Conduction by variable-range hopping in pseudo-one and two dimensions is expected to have $\ln\sigma \propto T^{-1/2}$ and $\ln\sigma \propto T^{-1/3}$, respectively[1,55,56]. The slightly smaller slope for a PA-PI film with a higher percentage of PA blocks seen in *Figure 8* may indicate that the density of the states at Fermi level, $N(E_F)$, increases only slightly with increasing in PA weight percentage for the copolymer films with polyacetylene content above the percolation threshold.

CONCLUSIONS

We have clearly demonstrated that soluble conducting copolymers of polyacetylene and polyisoprene synthesized by different catalysts under different conditions could have very different morphologies. The fairly strong correlation between the phase structure and charge transportation implies that electrical properties of the polyacetylene–polyisoprene copolymer materials may be controlled through modifications of their morphologic structures and/or syntheses.

I_2-doping of the polyacetylene and polyisoprene diblock copolymer films prepared by the cobalt catalyst in toluene has been shown to be accompanied by a phase transformation from a homogeneous state, through the worm-like micelles, to a thermoplastic pseudo interpenetrating polymer network (PIPN) at the micrometre scale; along with the formation of a rod-like structure of the I_2-doped polyacetylene chains at the nanometre scale. The phase separation behaviour was stemmed from the strong self-association of polyacetylene segments in conjunction with the thermodynamic immiscibiity between polyisoprene and the I_2-doped polyacetylene chains. The rod-like network formed in the I_2-doped PA-PI diblock copolymers seems to be an advantage for the materials to gain a low percolation threshold (*ca* 7 wt% $(CH)_x$). Furthermore, the doping-induced phase separation process may have potential implications for making various multiphase conducting polymers with different ordered structures ranging from the nanometre to the micrometre scale[57].

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APPENDIX A

Theoretical prediction of the critical Flory–Huggins segmental interaction parameter, $(\chi_{AB})_{cr}$

Theoretically, the conditions necessary for microphase separation in non-crystalline block copolymers or in mixtures of block copolymers with one of the corresponding homopolymers depend on the composition of the block copolymer, its molecular weight, the number of blocks per molecule, the Flory–Huggins segmental interaction parameter, χ, and the molecular weight of the added homopolymer. For monodisperse block copolymer samples, the lattice theory of solution[58] gives the enthalpy change on microphase separation when no crystallization occurs as follows[59]

$$\Delta H = -\frac{kTV}{V_{\mathrm{r}}}\nu_{\mathrm{A}}^{\mathrm{M}}\nu_{\mathrm{B}}^{\mathrm{M}}\chi_{\mathrm{AB}}\left(1-\frac{2}{z}\right) \qquad \text{(A1)}$$

where V is the total volume of the system; T is the absolute temperature; k is the Boltzmann constant; V_{r} is the volume of a lattice site; z is the coordination number of the lattice (for each non-end monomer unit in each polymer chain, only $z-2$ contacts are random before microphase separation, since two contacts are fixed by the composition of the chain); $\nu_{\mathrm{A}}^{\mathrm{M}}$ and $\nu_{\mathrm{B}}^{\mathrm{M}}$ are volume fractions of monomer repeat units A and B in the total mixture, respectively; and χ_{AB} is the Flory–Huggins interaction parameter between A units and B units.

Besides, equation (A2) gives the total entropy change provided that microphase separation occurs in the absence of crystallization, and the only contacts between A and B after microphase separation are A–B junctions within block copolymer molecules at the interface between microphases:

$$\frac{\Delta S}{k} = N_{\mathrm{c}}\ln(\nu_{\mathrm{A}}^{\mathrm{M}})^{\nu_{\mathrm{A}}^{\mathrm{C}}}(\nu_{\mathrm{B}}^{\mathrm{M}})^{\nu_{\mathrm{B}}^{\mathrm{C}}} + N_{\mathrm{HA}}\ln\nu_{\mathrm{A}}^{\mathrm{M}} - 2N_{\mathrm{c}}(m-1)\left(\frac{\Delta S_{\mathrm{dis}}}{R}\right) + N_{\mathrm{c}}\ln(m-1) \qquad \text{(A2)}$$

Here N_{HA} is the number of homopolymer molecules in the system; $\nu_{\mathrm{A}}^{\mathrm{C}}$ is the volume fraction of monomer A in the copolymer molecules; m is the number of blocks in each block copolymer molecule, which has a value of 2 in our case; and $(\Delta S_{\mathrm{dis}})/R$ is the disorientation entropy gain on fusion per segment of a polymer, which has values of range from 0.85 to 4.3 for various polymers[60]. Combination of equations (A1) and (A2) into $\Delta G = \Delta H - T\Delta S$, therefore, gives the free energy change on microphase separation for a system consisting of N_{c} copolymer molecules of A–B and N_{HA} homopolymer molecules of A.

Since $\Delta G = 0$ corresponds to a state at which a separated phase is in equilibrium with a completely mixed phase, solution of this equation allows calculation of critical values of the Flory–Huggins interaction parameter, $(\chi_{AB})_{cr}$. This critical value is the lowest value of the parameter for a particular multicomponent system to exhibit phase separation behaviour.

On the basis of the following relationships

$$V = N_c(V_A n_A^c + V_B n_B^c) + N_{HA} V_A n_{HA} \tag{A3}$$

and

$$\nu_A^M = \frac{N_{HA} V_A n_{HA} + N_c V_A n_A^c}{V} \tag{A4}$$

(where V_i and n_i^c represent the volume and the number of repeat units for unit i in each copolymer molecule, respectively; and n_{HA} is the number of A units in each homopolymer molecule), equation (A5) is obtained[59] which gives $(\chi_{AB})_{cr}$ for a block copolymer of A–B mixed with the corresponding homopolymer of A.

$$(\chi_{AB})_{cr} = \frac{zV_r}{(z-2)V_B \nu_A^M n_B^c}\Bigg[-\ln(\nu_A^M)^{\nu_A^c}(\nu_B^M)^{\nu_B^C} - \frac{N_{HA}}{N_c}\ln\nu_A^M + 2(m-1)\frac{\Delta S_{dis}}{R} - \ln(m-1)\Bigg] \tag{A5}$$

When using equation (A5) to make predictions, it has been suggested[59,61] to let $V_r = V_B$; $z = 8$; and a possible value of 1.0 for the $(\Delta S_{dis}/R)$.

By using $z = 8$, $(\Delta S_{dis}/R) = 1.0$, and the values of 0.9346 and 1.2 (g ml^{-1}) for the density of polyisoprene[6] and polyacetylene[1], respectively, we have calculated, from equation (A5), the $(\chi_{AB})_{cr}$ for the diblock copolymer of PA_{753}-PI_{8000} to be 0.1112, which is quite close to the corresponding values for polydeuterated styrene–polybutadiene diblock copolymers with similar overall molecular weights[62].