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ELECTRICAL CONDUCTIVITY OF POLY(BUTADIENE-CO-2-VINYL PYRIDINE) DIBLOCK COPOLYMERS DOPED WITH TCNQ

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Abstract—Diblock copolymers of various compositions consisting of polybutadiene blocks (PB) and poly(2-vinyl pyridine) blocks (P2VP) were prepared by anionic polymerizations. The P2VP block was converted to a polycation and reacted with 7,7,8,8-tetracyanoquinodimethane (TCNQ) while the PB block was left unchanged. Flexible and processible films of these block copolymers with conductivities as high as $10^{-2}\,\mathrm{Scm}^{-1}$ were cast from organic solvents. Conductivity measurements and wide angle X-ray diffraction results confirmed that there is an optimal ratio of TCNQ^0 to $\mathrm{TCNQ}^{\cdot-}$ for which the conductivities are highest. It was found that this ratio was somewhat higher than expected because of the reaction of TCNQ^0 adjacent to $\mathrm{TCNQ}^{\cdot-}$ anion-radicals and with the quaternized and unquaternized pyridine units. Transmission electron microscopy studies revealed the presence of essentially regular phase separation in the solid state of the simple salts of the block copolymers but phase separation in complex salts of the block copolymers was highly irregular.

INTRODUCTION

Many electrically conducting polymers which have been described to date have undesirable characteristics such as insolubility, intractability, poor processibility or in some cases low molecular weights. These properties are a severe disadvantage in practical applications. For these reasons, attempts have been made either to blend conducting polymers with conventional polymers [1] or to synthesize block or graft copolymers in which one of the blocks consists of a potentially conducting polymer [2] while the other block is a polymer which increases the solubility in organic solvents of the entire copolymer and improves processibility. Of principal interest in these studies are requirements for the formation of a continuous percolating phase of the conducting polymers, which is needed to achieve conductivity throughout the solid sample.

Among the conducting polymers studied to date, the poly(vinyl pyridine) polymers have been considered attractive because they could be reacted ("doped") with either iodine or TCNQ (7,7,8,8-tetracyanoquinodimethane) [3–8] to obtain semiconducting materials. Indeed poly(2-vinyl pyridine) (P2VP) doped with iodine is one of the few conducting polymers with commercial applications [9]. However, a major disadvantage of P2VP is its brittleness which increases after doping with TCNQ because of polymer ionicity. The present investigation is concerned with the electrical properties of poly(butadiene-co-2VP) diblock copolymers (BP) doped with TCNQ, and the correlations of these properties with the solid state morphology. Results from studies of temperature and environmental stability are also presented.

EXPERIMENTAL PROCEDURES

Polymer synthesis

Poly(butadiene-co-2VP) diblock copolymers with various compositions were prepared by anionic polymerization with n-butyl lithium as initiator. The details of the polymer synthesis are the subject of a separate publication [10].

Quaternization of P2VP block in BP

Quaternization of the P2VP block was carried out by reacting the sample with methyl iodide in tetrahydrofuran (THF) at *ca* 70° usually for 24 hr. It was important to use high purity THF (purified by distillation from sodium–benzophenone complex) because, when quaternization was performed in non-purified THF, it was found by elemental analysis that the sum of the C, H, N and I percentages differed from 100% by 5–8% suggesting that some other products were present. Quaternization of the P2VP homopolymer (h-2VP) was carried out in nitromethane as a solvent under the same conditions as for the BPs. Quaternized polymers were recovered by precipitation in methanol and dried at 40° under a pressure of *ca* 0.3/mbar. Since the polymers are highly hygroscopic, they were stored under an inert atmosphere.

Synthesis of poly(butadiene-co-1-methyl-2-vinyl pyridinium-TCNQ$^{\cdot-}$) simple salts [poly(Bu/2VP-Q-D)]

Poly(butadine-co-1-methyl-2-vinyl pyridinium iodide) was dissolved in dimethylformamide (DMF)–THF mixture and mixed with a solution of LiTCNQ (prepared by the method of Acker *et al.* [11]) in DMF at room temperature. The reaction mixture was stirred for 4 hr and the polymer was precipitated in water-free methanol. The precipitate was washed with a large amount of methanol, filtered in a glove bag and dried under vacuum. Samples were stored in an inert atmosphere.

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Film casting and formation of complex salts

A solution of the poly(Bu/2VP-Q-D) simple salt and the formally neutral TCNQ (TCNQ^0) in DMF–THF or DMF–xylene was cast in a flat glass dish which had been thoroughly cleaned in a base bath and then treated with dichlorodimethylsilane to facilitate film removal. Casting was carried out *in vacuo* over a seven day period and resulted in a black film of the poly(Bu/2VP-Q-DC) complex salt. Films *ca* 0.1–0.2 mm thick were typically used in this study.

Conductivity, morphology, temperature and environmental stability studies

Film samples, measuring *ca* 5 × 4 × 0.1 mm, were mounted in a four-probe conductivity measurement cell with colloidal graphite in methyl ethyl ketone (Electrodag). Conductivity was measured with a Data Precision electrometer.

Wide angle X-ray scattering was used to characterize the crystallinity of the complex salts. A CuK$_\alpha$ X-ray source was used with a Statton camera to obtain flat film diffraction patterns.

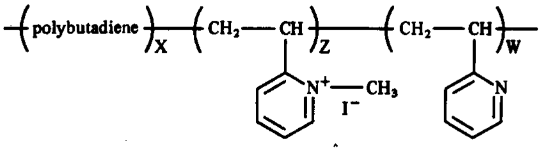
Morphology of the simple and complex salts in the solid state was studied by transmission electron microscopy (JEOL 100CX TEM) with samples microtomed at −90° with a Reichert FC-4 cryomicrotome equipped with a glass knife. Microtoming of samples of the complex salts was more difficult than that of the simple salts probably because of the high degree of crystallinity. Before microtoming, the films had been exposed to iodine vapor which forms a charge-transfer complex with nonquaternized pyridine in the P2VP block [12]. The presence of this iodine and the iodine left during the formation of simple salts was sufficient to provide good contrast for distinguishing two different phases in the films of the simple and complex salts.

Conductivity (σ) as a function of temperature was measured at low temperatures with a cell equipped with a Heli-Tran refrigerator (model T-3-110, Air Products and Chemicals, Inc.). Temperature stability of the samples was studied by TGA (Perkin Elmer) under N$_2$. Environmental stability of the doped samples was studied by measuring the conductivities in an open atmosphere at room temperature over a period of 60 days.

RESULTS AND DISCUSSION

The characteristics of the block copolymers used in this work are presented in Table 1. The block copolymers BP-2, BP-3 and BP-5 had bimodal molecular weight distributions because they were prepared under conditions that allowed some chain branching during the anionic polymerization of 2VP [10]. The other three copolymers were prepared under conditions where branching was prevented.

Quaternization with methyl iodide of the P2VP block in the block copolymers was not complete in all cases. A similar result was observed previously [13, 14] and was attributed to electrostatic and steric effects. The incompletely quaternized diblock copolymers have the general formula:



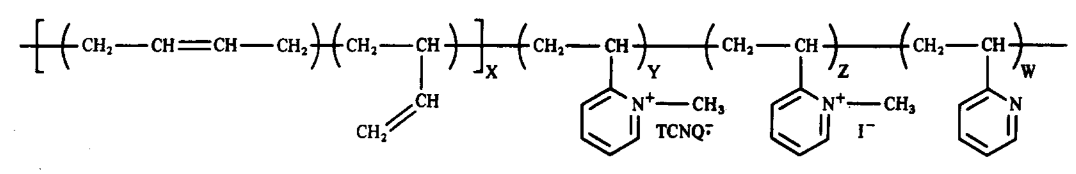
$$-\left(\text{polybutadiene}\right)_X-\left(CH_2-\underset{\underset{N^+-CH_3\ I^-}{|}}{CH}\right)_Z-\left(CH_2-\underset{\underset{N}{|}}{CH}\right)_W- \quad (1)$$

where X, Z and W are the mole fractions of the respective structural units. The degree of quaternization for these samples was calculated from the iodine/nitrogen ratio from elemental analysis, with the results given in Table 2. The highest degree of quaternization was found for h-P2VP (P-6) in nitromethane.

Results for the preparation of simple salts of poly(Bu/2VP-Q-D) are given in Table 3. The elemental analyses showed that all samples contained some residual iodine indicating that the exchange reaction:

$$\text{poly(Bu/2VP-Q)} + Li^+TCNQ^{\cdot-} \rightarrow \text{poly(Bu/2VP-Q-D)} + LiI \quad (2)$$

occurred on about every second pyridine unit. Thus the poly(Bu/2VP-Q-D) simple salts have the general formula:



$$-\left[\left(CH_2-CH=CH-CH_2\right)\left(CH_2-\underset{\underset{CH=CH_2}{|}}{CH}\right)\right]_X\left(CH_2-\underset{\underset{N^+-CH_3\ TCNQ^{\cdot-}}{|}}{CH}\right)_Y\left(CH_2-\underset{\underset{N^+-CH_3\ I^-}{|}}{CH}\right)_Z\left(CH_2-\underset{\underset{N}{|}}{CH}\right)_W- \quad (3)$$

where X, Y, Z and W are mole fractions of the respective structural units. The elemental analyses of the samples did not reveal the presence of even a trace of Li. It would also be very unlikely to find LiI in the samples because LiI is soluble in methanol which was used to precipitate the simple salts. From the elemental analyses, it was possible to calculate the values of X, Y, Z and W in equation (3) (Table 3).

The conductivities of the simple salts were all about 10^{-11} Scm^{-1}. Wide angle X-ray diffraction analysis (WAXR) of these salts showed that no crystalline structure was present. Figure 1 shows electron micrographs of the BP-2-Q-D, BP-3-Q-D, BP-4-Q-D and BP-5-Q-D simple salts. The films of BP-2-Q-D and BP-3-Q-D samples were obtained by casting from DMF–THF mixture while BP-4-Q-D and BP-5-Q-D films were cast from DMF–xylene (4/1, v/v). THF and xylene are good solvents for the polybutadiene block while DMF is good solvent for the poly(2VP-Q-D) block. In both cases, DMF remains as the last solvent during solvent removal and, since it is the preferential solvent for the poly(2VP-Q-D) block, this block forms a continuous phase while polybutadiene precipitates first forming spherical domains.

Conductivities of the complex salts showed dramatic increases and strong dependencies on the amount of TCNQ^0 present in the films, as can be seen from the results in Table 4 and Fig. 2. This dependency suggests that the TCNQ^0 molecules are associated with poly(2VP) cations forming stacks of alternating charged and neutral TCNQ^0 molecules,

Table 1. Characteristics of the poly(butadiene-co-2VP) block copolymers

Code	$\bar{M}_n \times 10^{-3}$				Wt% of P2VP	Vol comp.[c]	
	$\bar{M}_{n_1}(\bar{M}_{w_1}/\bar{M}_{n_1})$[a]	$\bar{M}_{n_2}(\bar{M}_{w_2}/\bar{M}_{n_2})$[a]	$\bar{M}_{n_1}^{P2VP}$[b]	$\bar{M}_{n_2}^{P2VP}$[b]		ϕ_{PB}	ϕ_{P2VP}
BP-1	140.70 (1.18)		22.20		15.80	0.87	0.13
BP-2	224.50 (1.06)	102.00 (1.09)	60.60	27.50	27.00	0.77	0.23
BP-3	165.30 (1.07)	68.44 (1.13)	54.07	22.40	32.70	0.72	0.28
BP-4	50.90 (1.08)		21.06		40.58	0.65	0.35
BP-5	126.70 (1.09)	40.10 (1.19)	68.90	26.20	54.40	0.51	0.49
P-6[d]	24.60 (1.05)		24.60		100.00	0.00	1.00

[a] Samples BP-2, BP-3 and BP-5 have bimodal molecular weight distributions. $\bar{M}_{n_1}$ and $\bar{M}_{n_2}$ are number average molecular weights of two different fractions.

[b] For the weight fractions: $X^{P2VP}:X^{PB} = \bar{M}_n^{P2VP}:\bar{M}_n^{PB}$.

[c] For the volume fractions: $\phi^{P2VP}:\phi^{PB} = \bar{M}_n^{P2VP}/d^{P2VD}:\bar{M}_n^{PB}/d^{PB}$ with bulk densities $d^{P2VD} = 1.114$ and $d^{PB} = 0.89$ g/ml.

[d] Sample P-6 is h-2VP.

similar to other cations [5, 15, 16]. The large difference between the conductivities of the simple and complex salts results from the different Coulomb energies for electron transfer between two TCNQ$^{\cdot-}$ molecules in the simple salts and TCNQ$^{\cdot-}$–TCNQ^0 in the complex salts. The effects of cations on conductivity has been discussed by LeBlanc [17] in terms of a simultaneous interaction of two electrons with a polarizable cation leading to the reduction of the Coulomb repulsion between electrons.

Table 2. Characteristics of the poly(butadiene-co-1-methyl-2VP iodide) block copolymers

Code	% of I	Degree of quaternization from I/N ratio (%)	X	Z	W
			according to equation (1)		
BP-1-Q	9.50	55.55	0.91	0.05	0.04
BP-2-Q	19.26	75.00	0.84	0.12	0.04
BP-3-Q	22.19	75.00	0.80	0.15	0.05
BP-4-Q	26.95	80.77	0.74	0.21	0.05
BP-5-Q	30.96	71.05	0.62	0.27	0.11
P-6-Q	50.68	95.00[a]	0.00	0.95	0.05

[a] h-2VP P-6 was quaternized in nitromethane.

Table 3. Characteristics of the poly(butadiene-co-1-methyl-2VP-TCNQ$^{\cdot-}$) simple salts

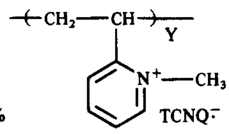
Code	Residual iodine (%)	X	Y	Z	W	Wt% PB	Wt% 
		according to equation (3)					
BP-1-Q-D	2.20	0.91	0.04	0.01	0.04	71.5	18.84
BP-2-Q-D	7.51	0.84	0.07	0.05	0.04	53.64	26.81
BP-3-Q-D	10.32	0.80	0.08	0.07	0.05	47.15	28.28
BP-4-Q-D	9.71	0.74	0.13	0.08	0.05	37.33	39.33
BP-5-Q-D	16.47	0.62	0.12	0.15	0.11	27.70	32.14
P-6-Q-D	18.97	0.00	0.53	0.42	0.05	0.00	61.20

Table 4. Characteristics of the poly(butadiene-co-2VP-Q-DC) complex salts

Code	Wt% TCNQ^0	$r = \frac{TCNQ^0}{TCNQ^{\cdot-}}$	r_{max}	Wt% PB	Wt% P2VP–TCNQ$^{\cdot-}$ TCNQ^0	Conductivity (Scm^{-1})
BP-1-Q-DC	10.60	0.96		64.0	27.4	$2.4 \cdot 10^{-4}$
BP-2-Q-DC	23.08	1.78		41.3	43.7	$4.6 \cdot 10^{-3}$
	16.30	1.15	1.30	44.9	38.8	$1.0 \cdot 10^{-2}$
	11.70	0.78		47.4	35.3	$3.4 \cdot 10^{-3}$
	0.00	0.00		53.6	26.8	$3.5 \cdot 10^{-11}$
BP-3-Q-DC	23.10	1.70		36.3	44.8	$2.8 \cdot 10^{-3}$
	16.00	1.07	1.25	39.6	40.0	$1.7 \cdot 10^{-2}$
	11.80	0.75		41.6	36.8	$1.5 \cdot 10^{-3}$
	0.00	0.00		47.2	28.3	$1.0 \cdot 10^{-11}$
BP-4-Q-DC	23.00	1.20		29.8	53.2	$2.1 \cdot 10^{-2}$
	16.30	0.78	1.25	31.3	49.2	$6.2 \cdot 10^{-3}$
	12.00	0.55		32.9	46.6	$7.0 \cdot 10^{-4}$
	0.00	0.00		37.3	39.3	$1.8 \cdot 10^{-11}$
BP-5-Q-DC	23.20	1.50		21.3	47.9	$1.5 \cdot 10^{-2}$
	16.40	0.97	1.50	23.2	43.3	$4.2 \cdot 10^{-3}$
	8.20	0.45		25.4	37.7	$2.2 \cdot 10^{-4}$
	0.00	0.00		27.7	32.1	$1.5 \cdot 10^{-11}$
P-6-Q-DC	43.50	2.00			78.1	$1.8 \cdot 10^{-2}$
	36.60	1.50			75.4	$2.9 \cdot 10^{-2}$
	27.80	1.00	1.40		72.0	$2.0 \cdot 10^{-2}$
	16.15	0.50			67.5	$1.5 \cdot 10^{-3}$
	0.00	0.00			61.2	$2.1 \cdot 10^{-11}$

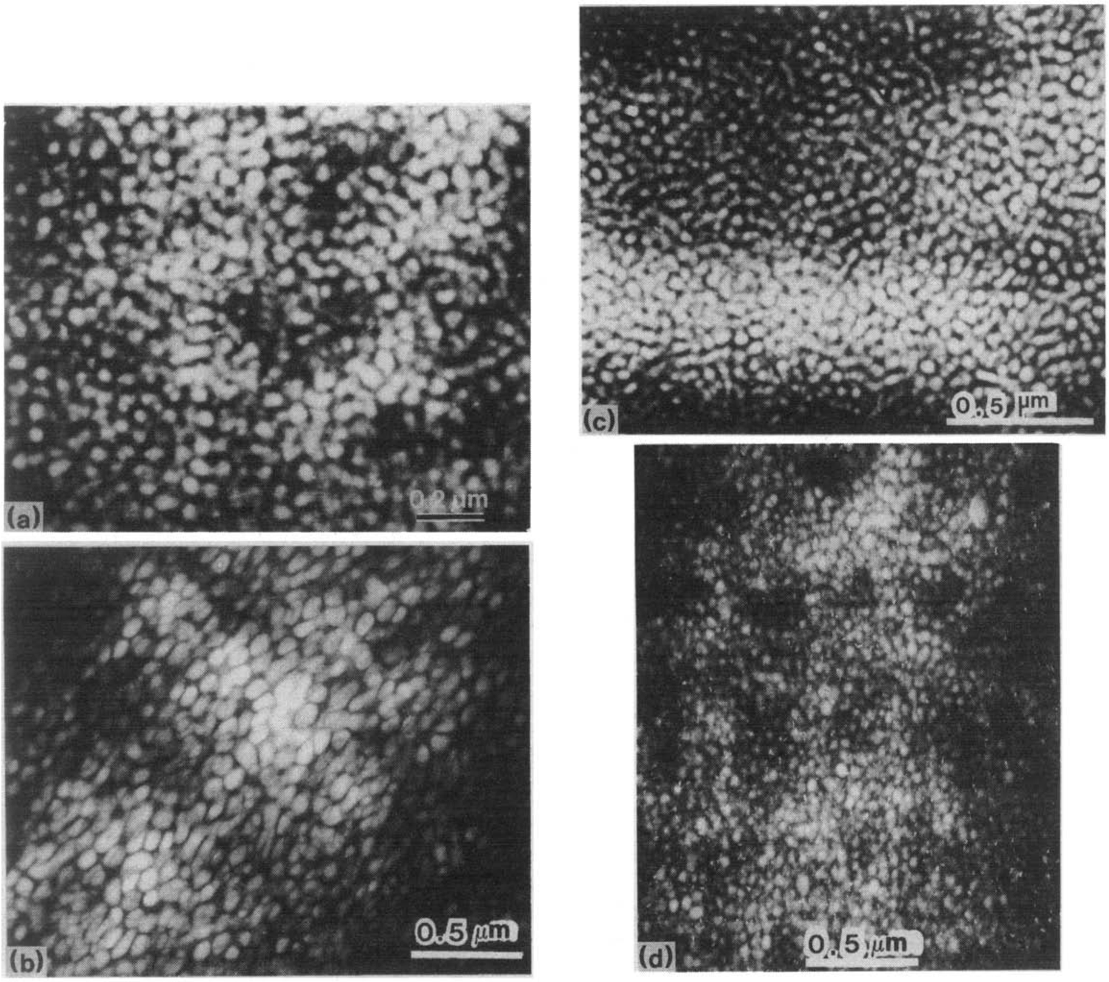


Fig. 1. Electron micrographs of BP-2-Q-D (a) and BP-3-Q-D (b) simple salts cast from DMF–THF mixture and BP-4-Q-D (c) and BP-5-Q-D (d) simple salts cast from DMF–xylene mixture.

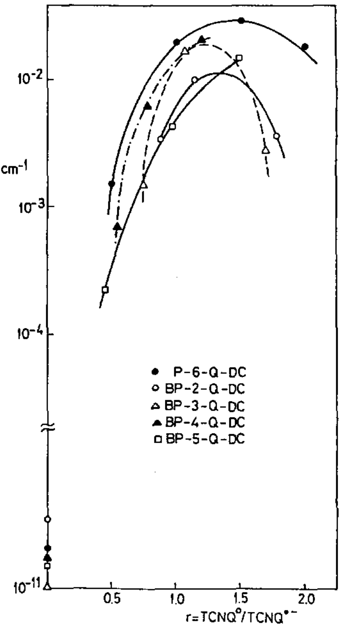


Fig. 2. Conductivity as a function of added neutral TCNQ⁰ for the indicated complex salts.

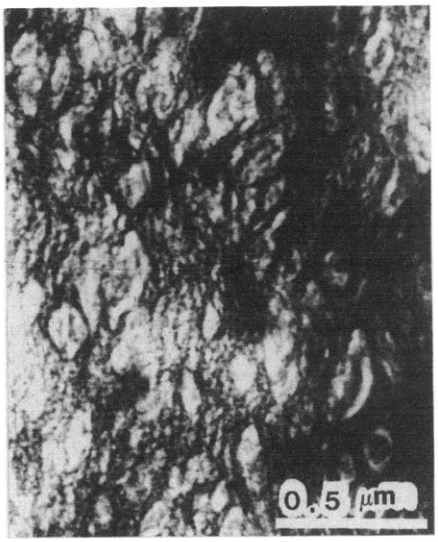


Fig. 3. Electron micrograph of BP-2-Q-DC complex salt with $r = 1.15$ cast from DMF–THF.

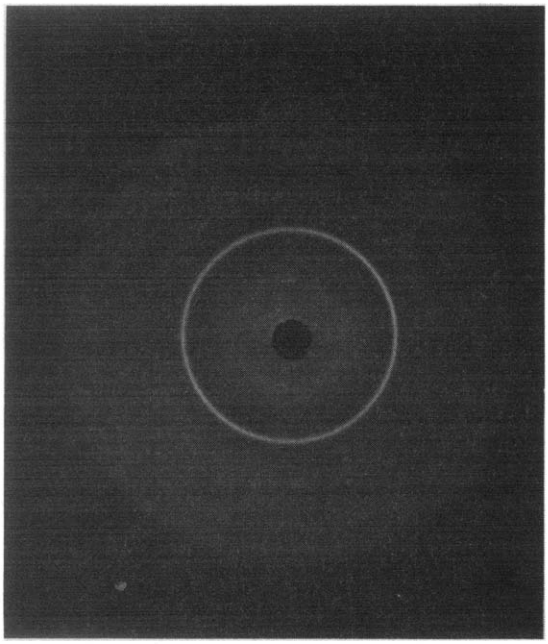


Fig. 4. WAXR diffraction pattern of the complex salts prepared in this work.

The electronic conductivity of these materials was confirmed by experiments in which current was passed through the samples for prolonged periods without detectable change in conductivity or observable polarization effects.

Transmission electron microscopy studies of the complex salts revealed "nonregular" phase separation of polybutadiene and poly(2VP)-doped blocks in terms of Molau's rule [18]. Figure 3 shows an electron micrograph of the BP-2-Q-DC complex salt containing 16.3 wt% $TCNQ^0$; it can be seen that the poly(2VP)-doped blocks make a continuous conducting phase while polybutadiene separates into irregular domains.

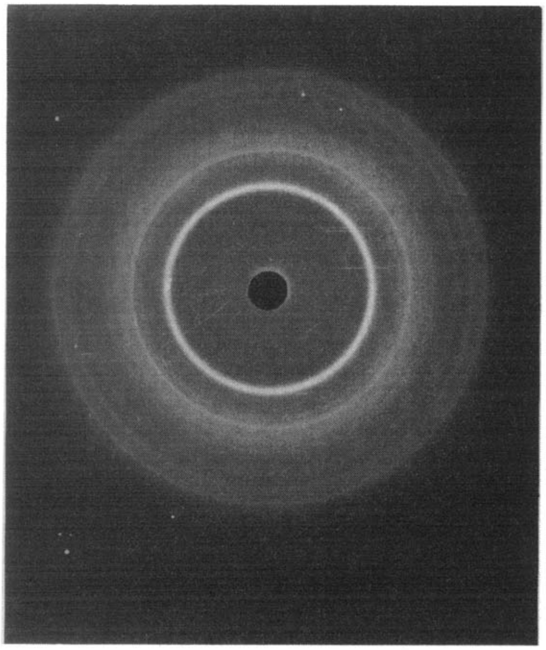


Fig. 5. WAXR diffraction pattern of the complex salts when $TCNQ^0$ was present in excess.

The crystalline structure of the poly(2VP) complex salt is not known. Figure 4 presents a Debye–Scherrer diffraction pattern of this salt with a reflection corresponding to a spacing of 0.62 nm, in agreement with the data by Lupinski *et al.* [4]. The same patterns were obtained for the BP-1- to BP-5-Q-DC complex salts, indicating that the polybutadiene phase was free of $TCNQ^0$. The curves in Fig. 2 show a maximum suggesting that there is an optimal amount of $TCNQ^0$ in the complex salts at which the conductivity is highest. When $TCNQ^0$ is present in excess, the conductivity decreases and the diffraction pattern of $TCNQ^0$ appears along with a reflection arising from the complex salt as seen in Fig. 5. It should be pointed out that the highest conductivities were observed for $r = TCNQ^0/TCNQ^-$ between 1.25–1.5, values which are higher than those found in other studies [4, 19] apparently because $TCNQ^0$ becomes associated with both unquaternized and quaternized pyridine units and because of some uncertainty in the amount of $TCNQ^-$ in the simple and complex salts.

The complex salts behaved as semiconductors obeying the relationship

$$\sigma(T) = \sigma_0 \exp(-\epsilon/Kt) \tag{4}$$

where ϵ is thermal activation energy. The results are shown in Fig. 6. The activation energy for conductivity of the P2VP complex salt (P-6-Q-DC) with $r = 1.50$ was calculated as 0.054 eV while activation energies of the block copolymer complex salts of BP-2-Q-DC, BP-3-Q-DC and BP-5-Q-DC were all *ca* 0.08 eV. The plots of $\log \sigma$ vs $1/T$ for the block copolymer complex salts show a break at *ca* −90°, below which the activation energy was somewhat lower. This temperature is quite close to the glass transition temperature of the polybutadiene phase

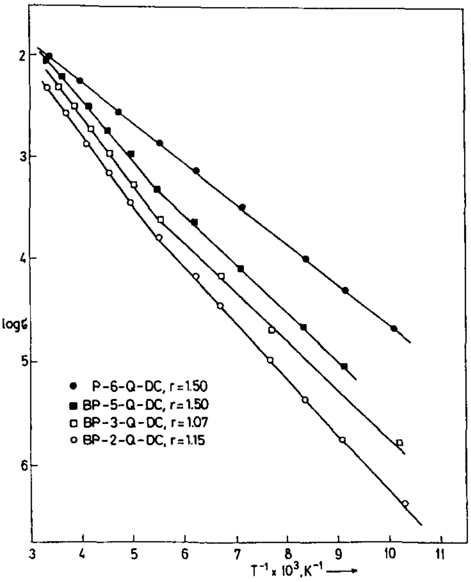


Fig. 6. Conductivity as a function of temperature of the indicated complex salts.

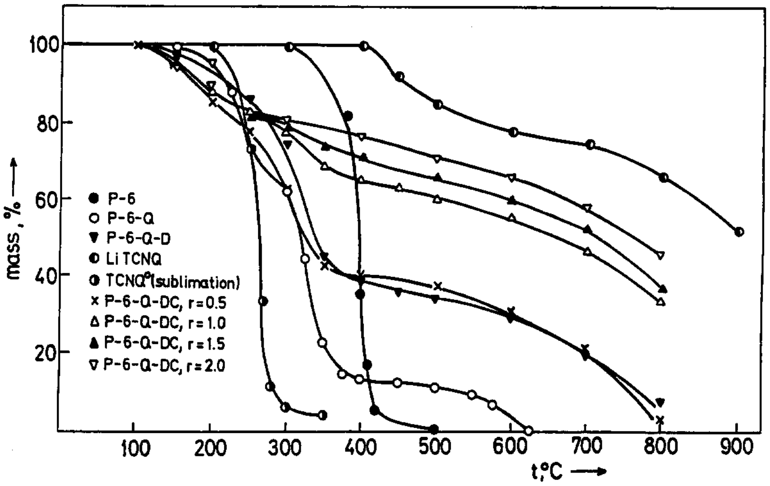


Fig. 7. Thermogravimetric analyses of the P-6-Q-DC complex salts and related compounds.

(−80°) which may be a coincidence since the polybutadiene phase is not expected to have a significant influence on the conductivity.

Figure 7 shows the results of thermogravimetric analyses of the P-6-Q-DC complex salts and related compounds. The degradation of the complex salts and quaternized P2VP starts between 100° and 150°, with elimination of methyl iodide. The presence of increasing amounts of TCNQ^0 (which in its pure state sublimes at *ca* 275°) increased the amount of complex salt formed and displaces the TGA curve to higher temperatures. This result and conductivity and X-ray diffraction results show that the complex salts are thermally quite stable and that they are not merely physical mixtures but result from a chemical interaction between the polymeric TCNQ salt and neutral TCNQ^0.

The chemical and electrical stabilities of polymeric TCNQ complex salts have been studied previously [20, 21]; it was found that TCNQ$^{\cdot-}$ in a complex salt decomposed to α,α-dicyano-*p*-toluoylcyanide as the final product and that water played an important part in the reaction. Figure 8 shows results of the conductivity change in an open atmosphere for some complex salts studied in this work. It can be seen that the conductivity of the complex salts decreases faster initially while at later times the slope of the σ-T curves remains constant. The conductivities of the block copolymer complex salts are somewhat less stable upon exposure to open atmosphere. This result may be attributed to the presence of the polybutadiene phase, which allows water to penetrate more quickly throughout the entire polymer sample. The change in conductivity observed is probably by the loss of unpaired electrons as a result of TCNQ^0 and TCNQ$^{\cdot-}$ disintegration [20].

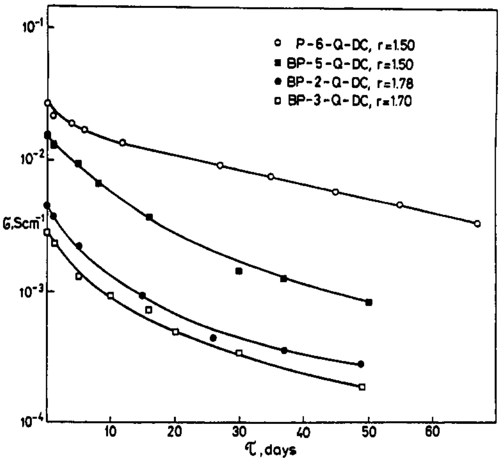


Fig. 8. Conductivity as a function of time in open atmosphere of the indicated complex salts.

CONCLUSION

(Bu/2VP-Q-DC) complex salts of various PB contents and exhibiting commercially interesting conductivities were prepared. The presence of a PB phase in these samples improved the mechanical properties. Films of samples of BP-1- to BP-3-Q-DC were highly flexible, while the films of BP-4- to P-6-Q-DC became increasingly brittle. All samples were soluble upon doping, and organic solvents such as DMF in small amounts were good plasticizers for these films.

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