Polymer Bulletin 23, 403–410 (1990)

Polymer Bulletin

Conductive radical anion salts of poly(butadiene-b-4-vinylpyridine) blockcopolymers

Sabine Kempf and Wolfram Gronski*

Institut für Makromolekulare Chemie der Universität Freiburg, Stefan-Meier-Strasse 31, D-7800 Freiburg, Federal Republic of Germany

SUMMARY

Poly(1,4-butadiene-b-4-vinylpyridine) blockcopolymers are made conductive by formation of the complex salt of the 4-VP-block with tetracyanoquinodimethane (TCNQ). Microphase separated morphologies are obtained where the conductive 4-VP phase is continous or forms a network on a submicron scale in a continous elastomer phase . While the absolute value of the conductivity of 10^{-3}-10^{-4} Scm^{-1} depends on the morphology the activation energy typical for an electron hopping process is approximately the same as in the low molecular weight complex with ethylpyridine.

INTRODUCTION

In addition to the conjugated polymers made conductive by doping with oxidizing or reducing agents polymers have gained a certain importance where the conductivity is achieved by incorporation of charge transfer complexes. This can be done by crystallizing low molecular weight charge transfer complexes as TTF/TCNQ (1) in an otherwise inert polymer matrix or by the formation of charge transfer complexes between a low molecular acceptor or donor and a polymer possessing functional groups with donor or acceptor functions (2). An example of this latter possibility are the radical anion salts of TCNQ with suitable polycations as polyvinylpyridine. As generally true for conductive polymers films of these polymeric complexes formed from solution are very brittle and therefore not very usefull for applications. A possibility to circumvent the inherent mechanical fragility of these systems is to prepare blockcopolymers having a rubberelastic and a conducting block.

In addition to the anticipated improvement of the film forming and mechanical properties it will be of interest to investigate the morphology of these systems and the influence of the morphoplogy on conductivity.

In this communication the preparation, morphology and electrical conductivity of poly(1,4-butadiene-b-4-vinylpyridine)

---

*To whom offprint requests should be sent blockcopolymers are described in which the 4VP block has been made conductive by quaternization with alkyl halides, subsequent reaction with the LiTCNQ salt and addition of neutral TCNQ. In a forthcoming paper the crystal structure of the polymeric complex and the model compound containing 4- ethylpyridine will be examined by X-ray analysis and scanning tunneling microscopy (3).

EXPERIMENTAL

A.Blockcopolymers

Polymer synthesis

Poly(1,4-butadiene-b-4-vinylpyridine) diblockcopolymers were prepared by anionic polymerization with sec-butyllithium as initiator. First butadiene was polymerized in benzene at 25° C. When the reaction was complete the reaction mixture was cooled down to 10° C and the 4VP monomer, diluted with tetrahydrofurane(THF) was added.

Quaternization of the 4VP block

Depending on the composition of the blockcopolymer two different routes have been taken. The blockcopolymer containing butadiene as the major component(80 wt%) was completely quaternized with methyl iodide in a THF/N,N-dimethylformamide(DMF) mixture at 50° C. Excess methyl iodide was removed under reduced pressure. Quaternization of a blockcopolymer with 50 wt% 4VP was carried out in a DMF/dimethylsulfoxide(DMSO) mixture with methyl iodide at 80° C for 10 h. After precipitation from excess acetone the quaternized product was dried under vacuum at ambient temperature.

Preparation of the polymeric $TCNQ^-$ salts

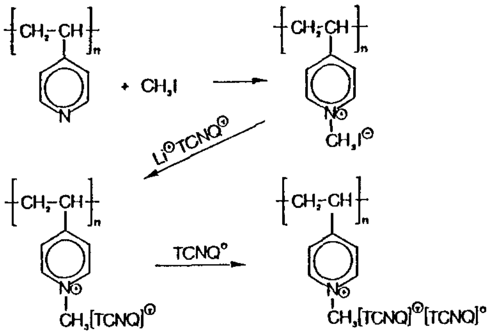
Because of the poor solubility of the blockcopolymer with 80 wt% butadiene after quaternization the reaction of this system with Li TCNQ was carried out in the same THF/DMF mixture used for quaternization. The solution of 1g of quaternized B4VP-5(B4VP-6) was mixed with 0.320 g of Li TCNQ dissolved in 100 ml of water. After the reaction mixture was concentrated under reduced pressure the resulting dark blue precipitate was filtered by pressure, washed with water,alcohol and ether and then dried in vacuum.

The reaction with the quaternized 50/50 blockcopolymer B4VP-2 was carried out by dissolving 1g of the sample in a mixture of 100 ml of water and 20 ml of THF. A solution of 0.560 g of LiTCNQ in 100 ml of water was added to the filtered polmer solution under stirring. A dark precipitate was formed immediately. It was worked up as described above.

$TCNQ^0$ doping of the polycation $TCNQ^-$ salts

The polymeric $TCNQ^-$ salts and neutral $TCNQ^0$ were combined in DMF. Homogeneous films of 150*10*0.3 mm^3 were cast from the solution at RT with a spin casting centrifuge. The resulting films could be removed without difficulty from the polyethylene terephthalate film with which the metal walls of the centrifuge were covered.

Reactionscheme:



B.Homopolymer

Polymer synthesis

Poly-4-vinylpyridine used in these experiments was prepared by azobisisobutyronitrile-initiated polymerisation in methanol at 50°C.

Quaternization

The purified polymer was quaternized with methyl iodide in ethanol at 30°C for 20 h. After removal of excess methyl iodide the polymer was poured into excess n-heptane. The precipitate was filtered and dried in vacuum.

Preparation of the polymeric $TCNQ^-$ salt

One gram of the fully quaternized polymer was dissolved in 200 ml of water. Then 0,860 g Li TCNQ dissolved in 200 ml of water were added to the polymer solution. After stirring for 20 min. the precipitate was filtered, washed with water and ether, and dried in vacuum.

$TCNQ^0$ doping of the polycation $TCNQ^-$ salt

The polymeric simple salt and neutral $TCNQ^0$ were combined in DMF, and films were cast as described for the blockcopolymers.

C.Model compound $4EP(TCNQ)_2$

Quaternization of 4-Ethylpyridine

4-Ethylpyridine was quaternized in DMF with methyl iodide at 60°C. After removal of the solvent and excess methyl iodide the product was purified by pouring an alcohol solution into excess ethyl acetate.

Preparation of the simple salt $4EP(TCNQ)_1$

A boiling solution of 0.496 g N-methylethylpyridinium iodide in 5 ml of ethanol was added to a boiling solution of 0.422 g of Li TCNQ in 100 ml of ethanol. The mixture was allowed to stand at 0°C for two days. The deep blue crystals were collected on a funnel, washed with iced ethanol, then with ether and dried in vacuum.

Preparation of the complex salt $4EP(TCNQ)_2$

A boiling solution of 0.650 g of the simple salt $4EP(TCNQ)_1$ in 25 ml acetonitrile was treated with a boiling solution of 0.500 g of $TCNQ^0$ in 30 ml of acetonitrile. The solution was kept at room temperature overnight. The resultant dark blue precipitate was filtered, washed with iced acetonitrile and dried in vacuum.

Table 1:

Sample	M_n / g/mol	wt%P4VP undoped	wt%P4VP[a] doped	σ_{300K}[b] / $\Omega^{-1}\,cm^{-1}$	E_a[b] / eV
B4VP-2	57000	52	79	$2.6\ 10^{-3}$	0.125
B4VP-5	494000	20	49	$1.9\ 10^{-4}$	0.110
B4VP-6	256000	20	48	$3.5\ 10^{-4}$	0.130
P4VP-12	110000	100	100	$7.6\ 10^{-3}$[c]	0.106
$4EP(TCNQ)_2$	-	-	-	$6.8\ 10^{-1}$[d]	0.098

[a] Calculated values for the P4VP $TCNQ^-TCNQ^0$-block

[b] Conductivity σ and activation energy E_a for $TCNQ^0$ doped polymers at 300 K

[c] Highest conductivity obtained for a homopolymer complex salt

[d] Powder conductivity

Characterization of the samples

The characterization of the blockcopolymers used in this investigation is contained in Table 1. The composition was determined by ^1H NMR. M_n was determined by osmometry. The extent of quaternization was estimated to be complete from IR by the disappearence of the pyridine band at 1595 cm^{-1} and the appearence of the absorption of quaternized pyridine at 1630 cm^{-1}.

Conductivity measurements

The measurements were carried out by the four probe method to eliminate contact resistance. Typical sample dimensions were $6*2*0.3$ mm^3. A Keithley 224 current source provided a constant current. The voltage was measured by a Keithley 617 electrometer. Specific resistivities and thermal activation energies were calculated from current-voltage characteristics measured in helium atmosphere in the temperature interval between 190 - 350°K.

Electron microscopy

Ultra thin sections were cut from the films using a LKB Cryo-Ultramicrotome. A Zeiss EM 902 microscope with integrated electron energy loss spectrometer was used for investigation of the morphology.

RESULTS AND DISCUSSION

Morphology

The elastic bright-field electron micrographs of ultrathin sections of the blockcopolymers B4VP-2 and B4VP-5 in Figs. 1 and 2 show the phase separation on a submicron scale. The morphology of the B4VP-2 sample is characterized by a coherent bright 4VP matrix in which dark polybutadiene particles of ca.200 Å diameter are embedded as expected from

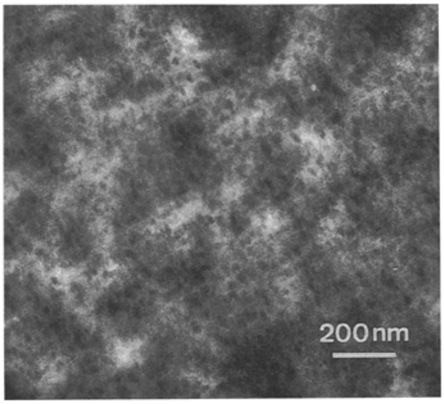


Fig. 1.B4VP-2,cast from DMF-solution at RT,stained by OsO_4,elastic bright field image

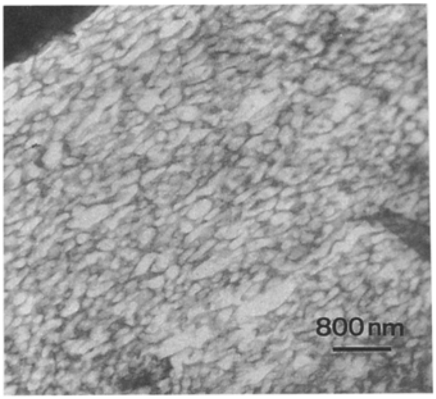


Fig. 2.B4VP-5,cast from DMF-solution at RT,uncontrasted,elastic bright field image

the composition of this blockcopolymer(see Table 1). The contrast in the EM picture is due to an exposure of the ultramicrotome section to OsO_4 vapor. The section of the B4VP-6 sample in Fig. 2 was not stained. The dark regions in this case originate from the microphase of the electron rich 4VP-TCNQ complex. According to the 50/50 wt% composition and the higher density of the semicrystalline P4VP phase a semicontinous or discrete morphology of the 4VP phase is expected. Instead the electron micrograph reveals a peculiar network-like structure of the 4VP phase embedded in the polybutadiene matrix. The width of the network strands varies from 100-1000 Å. The origin of this structure is considered to be due to the crystallization of the charge transfer complexes of the TCNQ moiety with the pyridine ring during evaporation of the solvent in the film casting process. The free energy of crystallization probably represents the main driving force for the phase separation in these systems. From similar charge transfer complexes of TCNQ with small organic donor molecules it is known that both acceptor and donor molecules crystallize in separate stacks. This basic structure was also found recently in the polymer complex by scanning tunneling microscopy (3). In the concentrated solution of the blockcopolymer where the complexes form the minor volume fraction as for the blockcopolymer considered this crystallization mechanism will favour the formation of small needle-like crystallites. Since the crystallization occurs under nonequilibrium conditions repeated nucleation at the crystallite surface leads to branching and eventually network formation. This mechanism is very similar to the nonequilibrium crystallization of small organic charge transfer complexes in polymer matrices during solvent evaporation (4). In the case of the crystallization of the 4VP-TCNQ complexes of the blockcopolymers considered here the crystallites are much smaller because the growth is restricted by the polybutadiene block.

Conductivity Measurements

Fig. 3 shows the conductivity of the two blockcopolymers versus temperature. The powder conductivity of the model compound 4-ethyl pyridine as well as the temperature dependence of the homopolymer conductivity are also shown for comparison. The B4VP-2 blockcopolymer showing a continous 4VP phase on the EM picture in Fig. 1 exhibits the higher conductivity of the two blockcopolymer samples. This is to be expected because a greater number of charge carriers per unit volume are present compared to B4VP-6 where the 4VP is the minor component. The magnitude of the conductivity of $2.6*10^{-3}\,Scm^{-1}$ at room temperature is not much different from the $TCNQ^-/TCNQ^0$ complex with poly(4-vinylpyridine)(see Table 1). The increase of the conductivity with increasing temperature is typical for n- semiconductors where the charge carriers(electrons) are generated by a thermally activated process. The activation energy of 0.106 eV reported for the complex of the homopolymer is of similar magnitude as for the complex of the blockcopolymer. The inclusion of dispersed polybutadiene particles therefore does not change the electrical properties of the system. On the other hand the film forming and mechanical properties are considerably improved by this modification. Attempts to produce films of the TCNQ⁻/TCNQ° complex of poly(4-vinylpyridine) of comparable surface area by spin casting failed. They generally desintegrate already after removal of the solvent or during the attempt to detach them from the support.

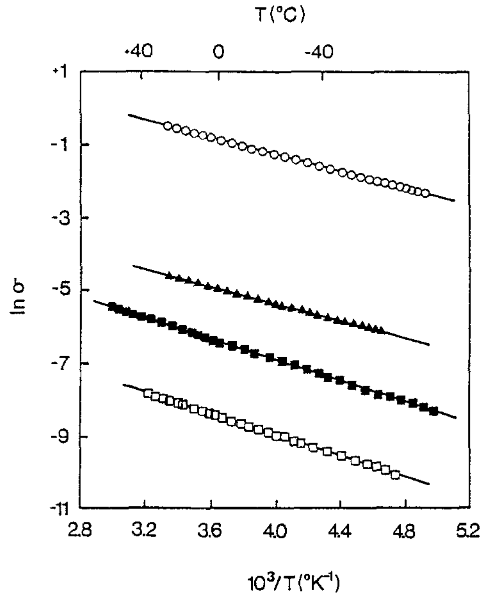


Fig. 3.Natural logarithm of the conductivity (in $\Omega^{-1}cm^{-1}$) versus inverse temperature for the complex salts : ○ 4EP(TCNQ)$_2$ ▲ P4VP-12 ■ B4VP-2 □ B4VP-6

The B4VP-6 blockcopolymer where the major phase is polybutadiene still exhibits a noticable conductivity of $3.5*10^{-4}$ Scm^{-1} at room temperature (*). The connective network of the 4VP phase seen in the EM picture of Fig. 2 generates a sufficient degree of percolation for electron transport. The decrease of conductivity with respect to the B4VP-2 sample by about one order of magnitude is considerably greater than the ratio of the volume fractions of the conductive component in the two blockcopolymers. One reason for this is directly apparent in the EM micrograph of Fig. 2. This shows that some of the conductive material of the 4VP phase is contained in electrically isolated cycles which are not connected to the micronetwork. Therefore the density of charge carriers must be less than that based on the brutto composition of the two blockcopolymers. Another reason for the reduced conductivity of B4VP-6 is probably due to a diminished mobility of the electrons due to a greater number of defects in the crystalline regions of the B4VP-6 microphase.

The activation energy of the conductivity is nearly the same in both cases independent of the vast differences in the morphological features of the two blockcopolymers. This result indicates that the observed activation energy is mainly determined by the electron hopping process within the crystalline regions of the 4VP microphase, i. e. by the crystal structure of the polymeric complex. The conductivity of a powder sample of the $TCNQ^-/TCNQ^0$ complex with 4-ethylpyridine has also been measured and is shown in the upper trace of Fig. 3. The absolute value is by a factor of 20 - 30 higher than in the B4VP blockcopolymers or 4VP homopolymer because of the higher crystallinity, i. e. the greater number of charge carriers. The activation energy of the model compound is lower than for the polymers. A comparison of the crystal structure of the model compound and of the complex in the polymer will answer the question whether the decrease of the activation energy has its origin in different interatomic distances in the TCNQ-stacks along which the electron transport occurs in both cases or in the higher degree of crystal perfection of the model compound.

The authors gratefully acknowledge the help of Dr. U. Heinrich with the EM measurement. The work was carried out in the SFB 60 of the Deutsche Forschungsgemeinschaft.

REFERENCES

(1) M.Kryszewski,J.K.Jeszka,J.Ulanski and A.Trasz
Pure & Appl. Chem., 56, 355 (1984)

(2) J.H.Lupinski,K.D.Kopple and J.J.Hertz
J. Polm. Sci., C16, 1561 (1967)

(3) to be published

(4) A.Trasz,J.Ulanski,M.Kryszewski
Polym. J., 15, 635 (1983)

(*) The conductivity measurements were performed on a material having the same composition as that shown in Fig. 2 but having a lower molecular weight of the unmodified blockcopolymer (see Table 1).The type of morphology is the same.

Accepted January 12, 1990 C