Highly Conducting, Soluble, and Environmentally-stable Poly(3-alkylthiophenes)

Kwan-Yue Jen, G. G. Miller, and Ronald L. Elsenbaumer

Polymer Laboratory, Allied-Signal Inc., Morristown, NJ 07960, U.S.A.

Homopolymers and copolymers of 3-alkylthiophenes incorporating alkyl groups equal to or greater than butyl in size can be handled in solution and form highly conducting, environmentally-stable compositions on doping.

Several poly(thiophenes)[1—4] have been reported to yield highly conducting complexes after exposure to acceptor dopants. However, total insolubility and non-meltability of these polymers prepared either by chemical or electrochemical methods means they cannot be processed using conventional techniques. We now report the synthesis and characterization of a series of melt mouldable poly(3-alkylthiophenes) which can be handled in solution to form highly conducting, environmentally-stable complexes with electron acceptor dopants.

Monomers 3-ethyl-, 3-n-butyl-, 3-n-octyl-thiophene, and 3,4-dimethylthiophene were prepared according to the procedure of Kumuda;[5] 3-methylthiothiophene was prepared according to Gronowitz *et al.*[6] The alkylthiophenes were iodinated by the method of Barker *et al.*[7] to give 3-alkyl substituted 2,5-di-iodothiophenes. Polymers were prepared by nickel catalysed Grignard coupling of the di-iodothiophenes, similar to the method used by Kobayashi *et al.*,[8] except that tetrahydrofuran (THF) and 2-methyltetrahydrofuran (2MTHF) were used as the reaction solvents. Random copolymers were prepared by the same procedure using different ratios of 2,5-di-iodo-3-methylthiophene and either 2,5-di-iodo-3-n-butylthiophene or 2,5-di-iodo-3-n-octylthiophene.

Homopolymers of 3-alkylthiophenes incorporating alkyl groups equal to or greater than butyl in size are readily soluble at room temperature in common organic solvents such as THF, 2MTHF, nitropropane, toluene, xylene, methylene chloride, anisole, nitrobenzene, benzonitrile, *etc.* Average molecular weights are in the range 3000—8000 as determined by vapour phase osmometry (v.p.o.) and end group analyses. I.r. and n.m.r. ($CDCl_3$) analyses on poly(3-butylthiophene) indicate exclusive coupling at the 2,5 positions with random regiospecificity (head-to-head, tail-to-tail, and head-to-tail). Solution cast (toluene) films are completely amorphous by *X*-ray.

Their deep red colour before doping ($\lambda_{max.}$ 460 nm) and high conductivity after doping with acceptor dopants (1—5 ohm^{-1} cm^{-1}, Table 1), clearly indicate that in spite of the large substituents, these polymers are extensively conjugated. Surprisingly, the conductivity of the doped, monoalkylated polymers is relatively insensitive to both the nature of the alkyl substituent and the dopant (see Table 1). In contrast, pristine poly(3,4-dimethylthiophene) is light yellow in colour and is much less soluble. Dialkylation presumably allows less extensive conjugation owing to increased steric interactions between adjacent thiophene rings compared to the monosubstituted thiophenes. The lower effective conjugation for this polymer raises its ionization potential relative to the monosubstituted polymers such that it is no longer doped by mild oxidizing reagents such as iodine. However, doping with reagents of greater electron affinity, such as nitrosylhexafluoroantimonate ($NOSbF_6$), results in a complex with a conductivity of 0.5 ohm^{-1} cm^{-1}. Electrochemically-prepared poly(3,4-dimethylthiophene) is reported to have a conductivity of 10 ohm^{-1} cm^{-1}.[9]

Table 1. Conductivities of doped poly(alkylthiophenes).

Polymer	Dopant	Doping level[a] (counterion)	Conductivity at 300 K (ohm^{-1} cm^{-1})
Poly(3-methylthiophene)	I_2	0.09 (I_3−)	3
	$NOBF_4$[b]	—	4
	$NOPF_6$[b]	—	4
	$NOSbF_6$[b]	0.15 (SbF_6−)	3
Poly(3-ethylthiophene)	I_2	—	3
Poly(3-n-butylthiophene)	I_2	—	4
	$NOSbF_6$[b]	0.14 (SbF_6^-)	0.1
Poly(3-methylthiothiophene)	I_2	—	0.5
Poly(3,4-dimethylthiophene)	$NOSbF_6$[b]	0.24 (SbF_6^-)	0.5
	I_2	—	—
Poly(3-methylthiophene–copolymer-3-butylthiophene) (50:50)	I_2	0.17 (I_3^-)	10[c]
	$FeCl_3$[b]	0.20 ($FeCl_4^-$)	50[c]
	$NOSbF_6$[b]	— (SbF_6^-)	18[c]
Poly(3-methylthiophene–copolymer-3-n-octylthiophene) (60:40)	$NOSbF_6$[b]	(—)	5

[a] Mole ratio of counterion to monomer repeat unit in the polymer as determined by elemental analyses. [b] Solutions in nitromethane. [c] Free standing films.

We have found that polymers with better film-forming properties (molecular weight *ca.* 35000, degree of polymerisation *ca.* 300) and higher conductivities are produced by random copolymerization of di-iodinated derivatives of 3-methylthiophene and 3-n-butylthiophene. Solubility at room temperature decreases and the glass transition temperature (T_g) increases as the content of 3-methylthiophene in the copolymer increases; T_g ranges from 48 °C for the homopolymer of 3-butylthiophene, to 60 °C for a 1 : 1 copolymer, to 145 °C for pure poly(3-methylthiophene). Amorphous, coherent films with good mechanical properties are obtained by solvent casting the 1 : 1 copolymer from toluene. Cast films, 38 µm thick, when treated at room temperature with an $FeCl_3$ solution in nitromethane–toluene (85 : 15) typically exhibit conductivities of 50 ohm^{-1} cm^{-1} (four-in-line probe technique). Homogeneous doping is evidenced by scanning electron microscope microprobe analysis for Fe.

As found for poly(3-methylthiophene),[10] acceptor-doped poly(3-alkylthiophenes) appear to be stable to water vapour (*i.e.* environmentally-stable). However, doped compositions containing halogenated anions (BF_4^-, PF_6^-, SbF_6^-, $FeCl_4^-$, I_3^-, *etc.*) do not possess high thermal stability. Thermogravimetric analyses indicate that compositions doped with these anions degrade with the liberation of neutral Lewis acid halides (BF_3, PF_5, I_2, *etc.*). The approximate order of thermal stability with relation to incorporated anion is: $SbF_6^- > FeCl_4^- > PF_6^- \sim BF_4^- > I_3^-$. The conductivity of an $FeCl_3^-$-doped copolymer film was found to degrade from 67 ohm^{-1} cm^{-1} to 16 ohm^{-1} cm^{-1} after ten months at room temperature. Elevated temperatures (100 °C) result in a more rapid loss in conductivity (by a factor of 2 in 24 h). Initial indications are that this conductivity loss is primarily due to dopant degradation and not polymer crosslinking since thermally compensated films remain flexible.

In spite of certain limitations, this class of conducting polymer promises to combine convenient processing and environmental stability with the mechanical properties needed for a variety of applications.

Received, 30th May 1986; Com. 729

References

1 T. Yamamoto, K. Sanechika, and A. Yamamoto, *J. Polym. Sci., Polym. Lett. Ed.*, 1980, **18**, 9.
2 K. Kaneto, Y. Kohno, K. Yoshino, and Y. Inuishi, *J. Chem. Soc., Chem. Commun.*, 1983, 382.
3 R. J. Waltman, J. Bargon, and A. F. Diaz, *J. Phys. Chem.*, 1983, **87**, 1459.
4 M. Sato, S. Tanaka, and K. Kaeriyama, *J. Chem. Soc., Chem. Commun.*, 1985, 713.
5 K. Tamao, S. Kodama, I. Nakajima, and M. Kumuda, *Tetrahedron*, 1982, **38**, 3347.
6 S. Gronowitz, P. Moses, and R. Hakansson, *Arkiv. Kemi.*, 1960, **16**, 624.
7 J. Barker, P. R. Huddleston, and M. L. Wood, *Synth. Commun.*, 1975, **5**, 59.
8 M. Kobayashi, J. Chen, T. C. Moraes, A. J. Heeger, and F. Wudl, *Synth. Metals*, 1984, **9**, 77.
9 G. Tourillon, D. Gourier, F. Garnier, and D. Vivien, *J. Phys. Chem.*, 1984, **88**, 1049.
10 G. Tourillon and F. Garnier, *J. Electrochem. Soc., Electrochem. Sci. Techn.*, 1983, **130**, 2043.