

Processible Conductive Copolymers of 3-Methylthiophene and Methyl Methacrylate

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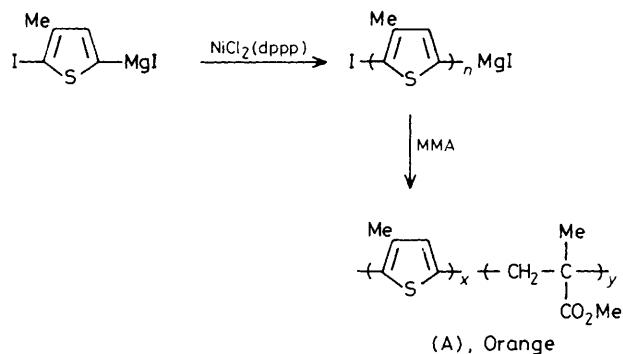
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Copolymerization of 3-methylthiophene and methyl methacrylate through two different reaction sequences generates two processible conductive copolymers which exhibit different optical, electrical, and electrochemical properties.

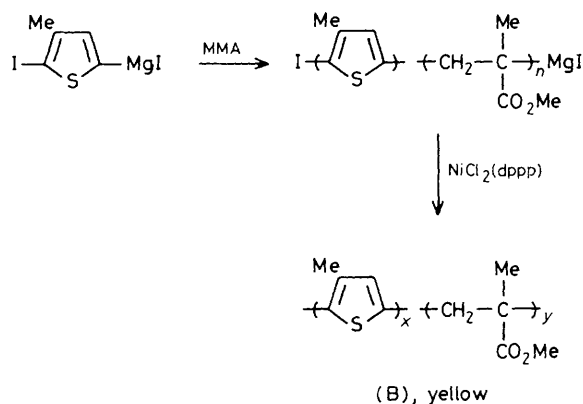
The recent interest in producing mechanically strong polyheterocyclic conducting polymers for potential technological applications has led to the preparation of composite materials containing conducting polymers like polypyrrole and nonconducting polymers like poly(vinyl chloride)¹ or poly(vinyl alcohol).² Similarly, composites of poly(3-methylthiophene) (PMT) and poly(methyl methacrylate) (PMMA) were also reported recently.³ Although these composites are electrically conductive with a mechanical strength similar to that of conventional polymers, their drawbacks include their heterogeneity due to the mixing of two different components and their lack of solution-processibility due to the existence of the insoluble conducting polymer portion. We now report the synthesis of random (block) copolymers of 3-methylthiophene and methyl methacrylate, providing the first example of solution-processible polymers of this type, combining electrically conductive polymer and conventional polymer units within a single polymer species. Although derivatives of

polythiophene like poly(3-methoxythiophene)⁴ and poly(alkylthiophenes)^{5,6} (substituents larger than methyl) were found to have improved solution-processibility, copolymerization of poly(alkylthiophenes) with conventional polymers provides a new approach in making processible conducting polymers whose properties are suitable for a much larger variety of possible modifications than those derivatives mentioned above.

Iodination of 3-methylthiophene by the method of Barker *et al.*⁷ gave 2,5-di-iodo-3-methylthiophene, the reaction of which with magnesium in tetrahydrofuran solution gave the Grignard monomer. Copolymers of 3-methylthiophene and methyl methacrylate were synthesized under two different polymerization conditions (Schemes 1 and 2). Copolymer (A) was synthesized as in Scheme 1. The block PMT polymer was obtained by Grignard coupling between 5-iodo-4-methyl-2-thienylmagnesium iodide under conditions similar to those described by Jen *et al.*⁶ and Kobayashi *et al.*,⁸ except that a



Scheme 1. Synthesis of copolymer, method (A). dppp = $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$; MMA = methyl methacrylate.



Scheme 2. Synthesis of copolymer, method (B).

short polymerization time (~ 2 h) was used. Methyl methacrylate was then added to the system to form a random copolymer of 3-methylthiophene and methyl methacrylate. The incorporation of methyl methacrylate into the polymer chain was initiated by the Grignard reagent. This polymerization of methyl methacrylate by Grignard reagents was reported by Good⁹ and Nishioka¹⁰ as early as 1960. Copolymer (A) obtained as in Scheme 1 is orange. Elemental analyses indicated a ratio of 3-methylthiophene to methyl methacrylate of $\sim 2:1$. The average molecular weight of the polymer synthesized without any further purification was >2000 as determined by vapour phase osmometry in toluene solution. The transmission i.r. spectrum of the copolymer was a superposition of the individual i.r. spectra of the two parent polymers. The existence of syndiotactic PMMA in the polymer was identified by the presence of an absorption band near 1060 cm^{-1} which is missing from the spectrum of the isotactic polymer. Copolymer (B) was synthesized as in Scheme 2. The Grignard monomers acted as initiators for the polymerization of methyl methacrylate before they were allowed to couple with each other. Copolymer (B) is yellow; elemental analyses indicated that the ratio of 3-methylthiophene and methyl methacrylate is also $\sim 2:1$. As shown in Figure 1, the optical spectrum of copolymer (A) exhibits an absorption maximum at $\sim 380\text{ nm}$ with the edge tailing down to 550 nm , indicating that certain poly(3-methylthiophene) blocks were incorporated in each polymer chain. On the other hand, the spectrum of copolymer (B) shows only a small shoulder in this region, suggesting that 3-methylthiophene units were mainly separated by methyl methacrylate units.

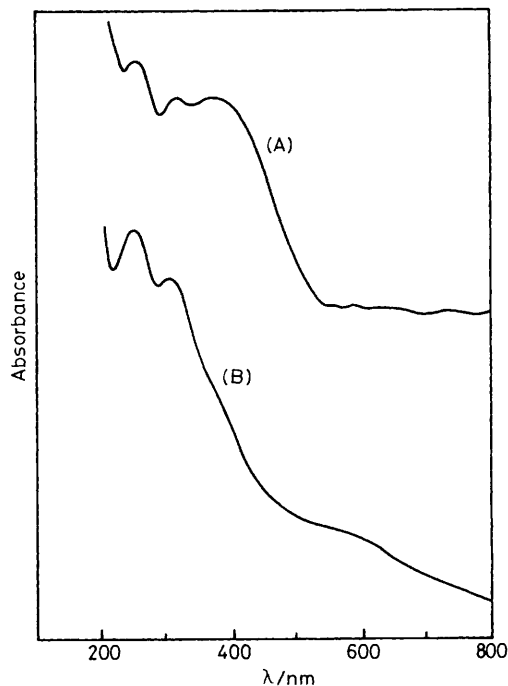


Figure 1. Optical spectra of 3-methylthiophene and methyl methacrylate copolymers (A) and (B).

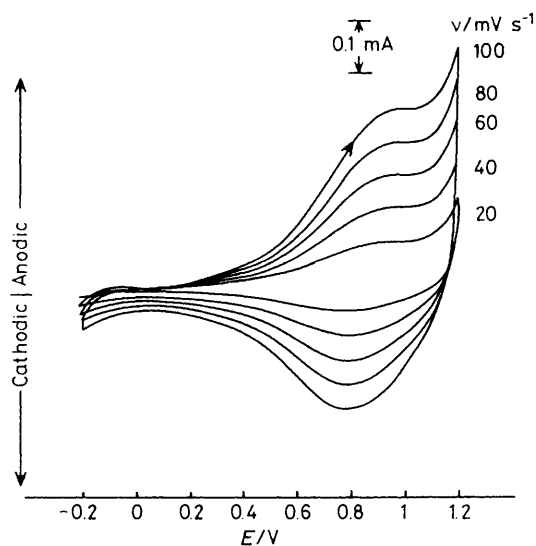


Figure 2. Cyclic voltammogram of chemically made poly(3-methylthiophene-methyl methacrylate) copolymer (A) on Pt foil ($\sim 1\text{ cm}^2$) in $0.1\text{ M LiClO}_4\text{-MeCN}$ at different scan rates between -0.2 and 1.2 V (vs. sodium chloride saturated calomel electrode).

Neither of the two abovementioned polymers exhibits any absorption peaks in the $800\text{--}2600\text{ nm}$ region.

It has been reported that both chemically⁵ and electrochemically¹¹ prepared PMT is not solution-processible. However, copolymer (A) and copolymer (B) are soluble in tetrahydrofuran (THF) and chloroform. Copolymer (A) is also soluble in toluene, but copolymer (B) is less soluble. This processibility is one of the advantages in this copolymer system which is not possible for the composites of PMT and PMMA. Since the

polymers are soluble, thin polymer coatings on Pt electrodes can be prepared for electrochemical studies. First, polymer solutions (in THF) were painted on Pt-foil electrodes ($\sim 1 \text{ cm}^2$), and then the electrodes were allowed to dry in air for ~ 30 min. These Pt electrodes containing thin polymer films were then subjected to a dynamic vacuum for more than 16 h pumping to remove residual solvent. Weights of the Pt electrodes were measured before and after the above treatment to obtain the amount of polymer coating. Cyclic voltammograms of copolymer (A) ($\sim 0.075 \text{ mg}$) shown in Figure 2 reveal a set of reversible redox waves, which indicate that the polymer is still electroactive, owing to the existence of PMT blocks in copolymer (A). On the other hand, the very few thiophene-thiophene linkages in copolymer (B) make it lose electroactivity completely. Electrical conductivities of iodine-doped copolymer (A) and copolymer (B) are 0.01 and 10^{-5} S/cm respectively. Since each polymer chain in the copolymer contains nonconducting methyl methacrylate units which will block the electron transport along the polymer chain, the conductivity will arise mainly from the overlapping of the conducting segments (percolation type). Thus, a higher proportion of 3-methylthiophene units in the copolymer should lead to higher conductivity. This is in fact the case, since copolymerization of 3-methylthiophene and methyl methacrylate in a 10:1 ratio by the method in Scheme 1 generates a copolymer which after iodine doping gives a conductivity of 0.2 S/cm.

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