# Chemical modification of poly(2,6-dimethyl- 1,4-phenylene oxide) by electrophilic substitution reaction with isocyanates*

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Summary
        The chemical modification of poly(2,6-dimethyl- 1,4-phenylene oxide) (PPO) has been carried out by incorporating amide groups on PPO backbone by electrophilic substitution reaction with isocyanates. The modified polymers obtained have been characterized by IR and ^{1}H-NMR spectroscopy, nitrogen analysis, solubility tests and X-ray diffraction studies.

Introduction
        Polymer modification is a rapidly expanding field of polymer science. The modification of existing synthetic and naturally occuring polymers is intended to improve some of their properties such as enhanced thermal stability, flexibility, solubility and so on.    Poly(2,6-dimethyl- 1,4-phenylene oxide) (PPO), one of the most widely used engineering plastics, has been modified by side chain bromination (1-3), phosphorylation (2-4), vinylation (5), carboxylation (6-7) and Friedel-Crafts reaction (8) such as acylation and sulfonylation.

        We report herein the modification of PPO by incorporation of amide groups on PPO aromatic units by electrophilic substitution reaction with isocyanates in the presence of aluminium trichloride.    This modification leads to a series of random copolymers as shown in the following reaction scheme.



Where  R = $C_6H_5-$ , $CH_3(CH_2)_2-$ , $CH_3(CH_2)_3-$
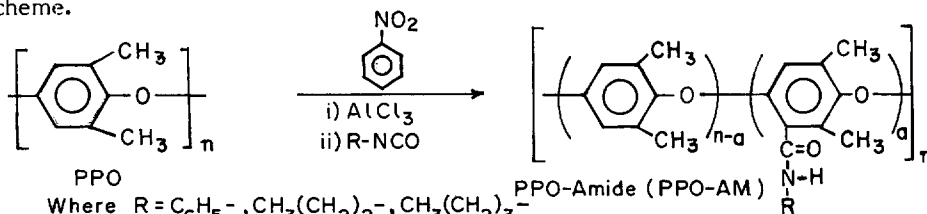
Preliminary characterization data such as IR and ^{1}H-NMR spectra, percent nitrogen, solubility and X-ray diffraction has been presented for these copolymers.

        The aim of these investigations is to use these modified polymers as membrane materials for gas separation as well as for desalination and to study the miscibility behaviour of blends of PPO-amide with polystyrene, nylons, etc.   Further, these modified polymers are interesting in their own right since they can be modified further to PPO-acid and various carboxylate derivatives such as esters, anhydrides, salts, etc. These studies will be reported in subsequent papers.

Experimental

Materials : PPO was synthesised according to a literature procedure(9). The measured intrinsic viscosity was 0.55 dl/g (CHCl$_3$, 30°C). Phenyl isocyanate (98%), butyl and propyl isocyanate (98%) were obtained from M/s. Fluka and Aldrich Chemical Co. respectively. AR grade anhydrous aluminium trichloride was used as received. All the solvents were distilled prior to use.

Synthesis of PPO-AM : All the experiments have been carried out at fixed concentration of PPO (1 mol), isocyanate (1 mol) and aluminium trichloride (1.1 mol). A mixture 5.0 g of dried PPO and 60 ml of nitrobenzene was placed in 250 ml round bottom flask fitted with a mechanical stirrer, a thermowell and a nitrogen gas inlet. PPO was dissolved under dry nitrogen stream at 80°C and required amount of aluminium trichloride was added. After the catalyst was dissolved the calculated amount of isocyanate was added gradually over a period of 15 minutes with constant stirring. The reaction was continued further for a fixed period as shown in Table 1. At the end of reaction, polymers PPO-AM1 and PPO-AM2 were isolated by breaking the aluminium trichloride complex by adding the reaction mixture dropwise into acidulated methanol and finally washed with distilled water till acid free. Since polymers PPO-AM3 to PPO-AM6 were found to be soluble in methanol, they were precipitated in petroleum ether (60-80°). The polymers were filtered off and subsequently suspended in acidified water (5 volume % HCl) for 3-4 h. They were washed with additional acidified water and finally with distilled water, till acid free. All the polymers were vacuum dried at 80°C to constant weight.

Techniques : The IR spectra were recorded on a Pye Unicam SP-3 300 spectrophotometer. The $^1$H-NMR spectra were recorded on a varian FT-80A instrument. The percent nitrogen was estimated by Dumas method. The X-ray diffractograms were obtained with a Phillips X-ray unit (Phillips generator, PW-1730) and a Ni filtered CuK$_\alpha$-radiations.

Results and Discussion

Amides are formed from the reaction of aromatic hydrocarbons with isocyanates in the presence of Friedel-Crafts catalyst such as aluminium trichloride (10).

$$R-N=C=O \xrightarrow{AlCl_3} R-N=\overset{\delta+}{C}\cdots\overset{\delta-}{O}\cdots AlCl_3 \xrightarrow{ArH} Ar-CONH-R$$
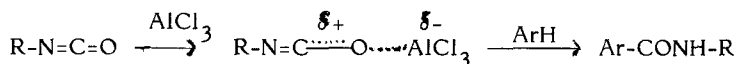
A similar electrophilic substitution reactions are expected to take place on PPO backbone due to high nucleophilic centres present in the tetra-substituted aromatic units. As the complex formation between isocyanate and aluminium trichloride requires an equivalent quantity of metal halide a slight excess over molar equivalent of aluminium trichloride has been used for the reaction of PPO with isocyanates. The excess of aluminium trichloride will serve as a catalyst.

Table 1 presents the experimental conditions used for the electrophilic substitution reaction of isocyanates on PPO backbone and molar degree of substitution determined by $^1$H-NMR spectroscopy and from the percent nitrogen.

Table 1

Modification of PPO with isocyanates

| Polymer | Isocyanate | Time h | Temp. °C | % nitro- gen | Molar degree of substitution (from % nitro- gen) | Molar degree of substitu- tion (from $^1$H-NMR) |
|---------|-----------|--------|----------|--------------|--------------------------------------------------|-------------------------------------------------|
| PPO-AM1 | $C_6H_5NCO$ | 5 | 80 | 3.95 | 0.51 | 0.50 |
| PPO-AM2 | $C_6H_5NCO$ | 10 | 80 | 4.25 | 0.57 | 0.56 |
| PPO-AM3 | $CH_3(CH_2)_2NCO$ | 5 | 80 | 4.18 | 0.48 | 0.50 |
| PPO-AM4 | $CH_3(CH_2)_2NCO$ | 10 | 80 | 4.43 | 0.52 | 0.54 |
| PPO-AM5 | $CH_3(CH_2)_3NCO$ | 5 | 80 | 4.13 | 0.50 | 0.51 |
| PPO-AM6 | $CH_3(CH_2)_3NCO$ | 10 | 80 | 4.58 | 0.58 | 0.57 |

Typical $^1$H-NMR spectra of PPO and PPO-AM polymers are presented in Figure 1 together with the assignment of their proton resonances. Multiple resonances for the methyl groups of the modified polymers should be due to the sequence distribution of the structural units. In the NMR spectrum of phenyl isocyanate modified PPO, (Figure 1 b), the amide-NH could not be assigned since it was merging with aromatic proton resonances.

The molar degree of substitution of the PPO aromatic units was determined from the ratio of the integrals of proton resonances due to unsubstituted 2,6-dimethyl- 1,4-phenylene units (signal $H_b$ at $\delta$ =6.40 ppm) and substituted units [signal $H_c$ at $\delta$ =6.10 (Figure 1b) and signal $H_c$ at $\delta$ =6.02 (Figures 1c and 1d)].
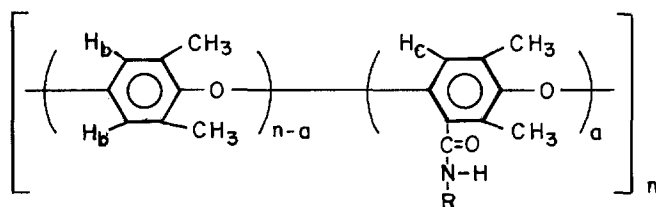


The following relationship has been used to claculate the molar degree of substitution.

$$\text{Molar degree of substitution} = \frac{Ic}{Ic/2 + Ib}$$

Where Ib and Ic represents the integrals of protons designated as 'b' and 'c' in the Figures 1b, 1c and 1d respectively.

The presence of electron withdrawing carbonyl group of the amide linkage attached to a PPO aromatic unit decreases the nucleophilicity of the unsubstituted position, hence no disubstitution of aromatic units was observed. At the same time unreacted positions are screened by the bulky
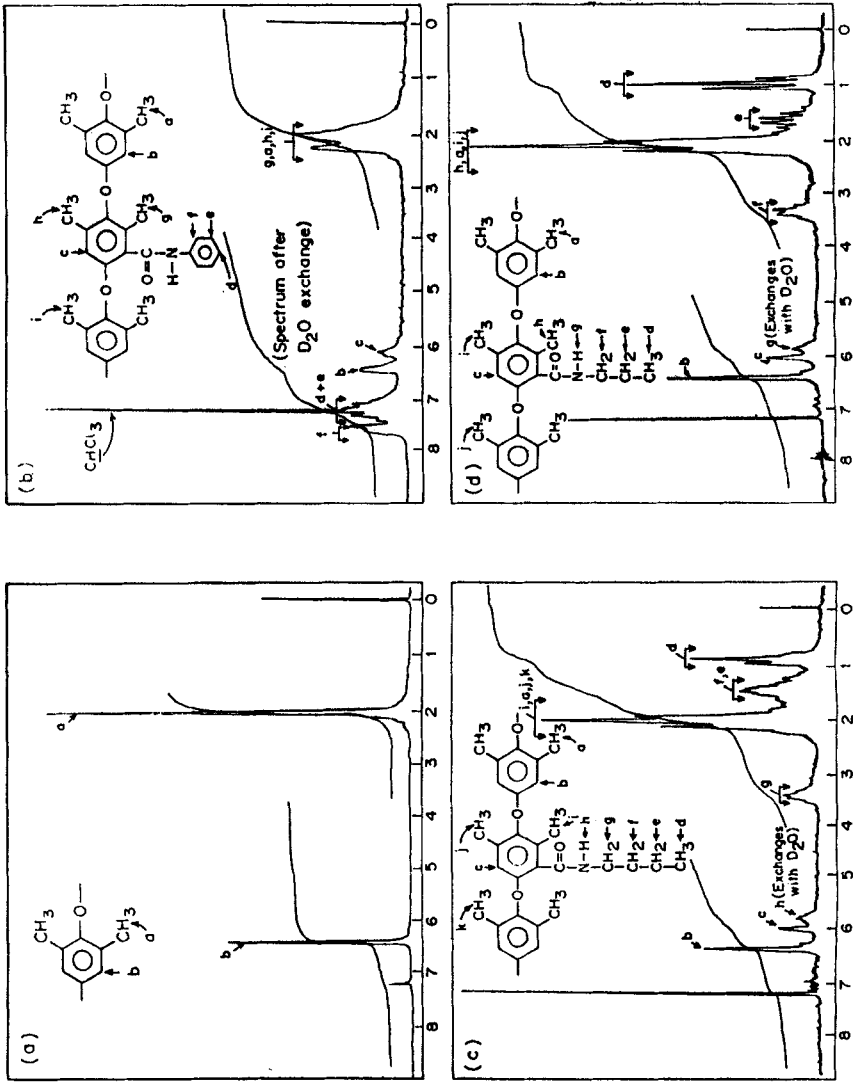
FIGURE 1 : $^1$H NMR SPECTRA OF PPO(a), PPO MODIFIED WITH PHENYL ISOCYANATE(b), PPO MODIFIED WITH BUTYL ISOCYANATE(c), AND PPO MODIFIED WITH PROPYL ISOCYANATE (d)

substituents and thus the steric effect makes the unreacted positions un-accessible. In all the cases, monosubstitution was demonstrated by measuring the ratio between the integrals of the unsubstituted aromatic proton of the substituted phenylenic units and some representative protons from the newly attached pendant groups. For example, the ratio between the signals c and f from spectrum (Figure 1b) and the ratio between the signals c and g from spectrum (Figure 1c) and c and f from spectrum (Figure 1d) were used to demonstrate monosubstitution.

The molar degree of substitution has also been calculated from the percent nitrogen, by using the following equation.

$$\frac{14\ X}{120 + XM} = \frac{Y}{100}$$

Where  M = molecular weight of isocyanate used
       X = molar degree of substitution
       Y = percent nitrogen estimated

The molar degree of substitution obtained by ^{1}H-NMR spectra and from percent nitrogen is in good agreement.

Figure 2 represents some typical IR spectra of parent PPO and iso-cyanate modified PPO samples. The attachment of pendant amide groups in the isocyanate modified PPO samples was confirmed by the presence of bands at 3320 cm$^{-1}$ and 1650 cm$^{-1}$ due to -NH stretching and  C=O stretch-ing vibrations, respectively.

Table 2

Solubility of PPO and isocyanate modified PPO

| Polymer | Solvent | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Nitro-ben-zene | Chlo-roform | DMF | DMSO | NMP | DMA | Meth-ylene chlo-ride | Ace-tone | Eth-anol | Meth-anol |
| PPO | + | + | − | − | − | − | ± | − | − | − |
| PPO-AM1 | + | + | + | + | + | + | + | − | − | − |
| PPO-AM2 | + | + | + | + | + | + | + | − | − | − |
| PPO-AM3 | + | + | + | + | + | + | + | + | + | + |
| PPO-AM4 | + | + | + | + | + | + | + | + | + | + |
| PPO-AM5 | + | + | + | + | + | + | + | + | + | + |
| PPO-AM6 | + | + | + | + | + | + | + | + | + | + |

+ = Soluble,  − = Insoluble,  ± = Tendency of crystallization.

Table 2 presents the solubility characteristics of isocyanate modified PPO. Unlike parent PPO, these polymers are soluble in dipolar aprotic solvents like dimethyl sulfoxide (DMSO), N,N-dimethyl formamide (DMF) and N,N-di-methylacetamide (DMA), which are conventional solvents for the preparation
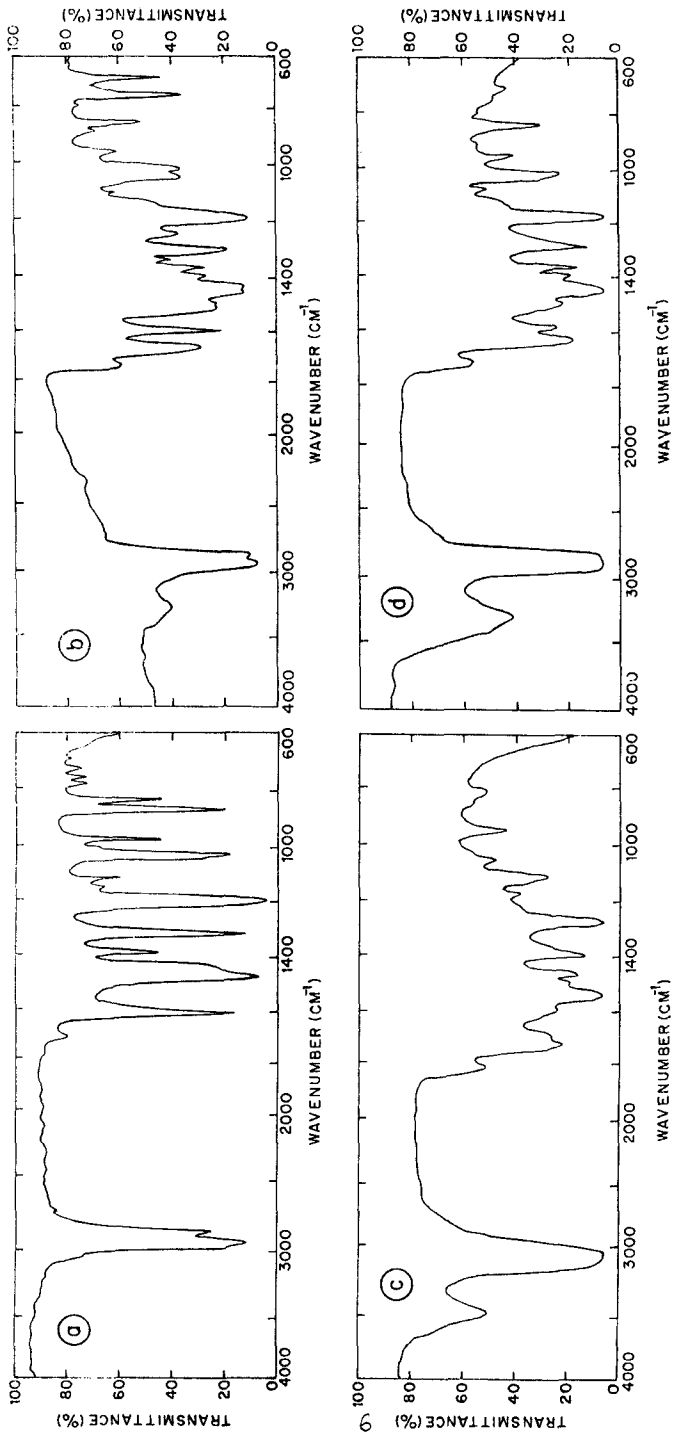
FIGURE 2 : IR SPECTRA OF PPO (a), PPO MODIFIED WITH PHENYL ISOCYANATE (b) ;
PPO MODIFIED WITH BUTYL ISOCYANATE (c); AND PPO MODIFIED WITH
PROPYL ISOCYANATE (d).

of asymmetric membranes. The broad range of solvents available for modified PPO enhances the possibility of casting films as polymer membranes from a large number of solvents. Like sulfonylated and acylated PPO polymers (8), PPO-AM polymers do not crystallize from methylene chloride and form stable solutions.
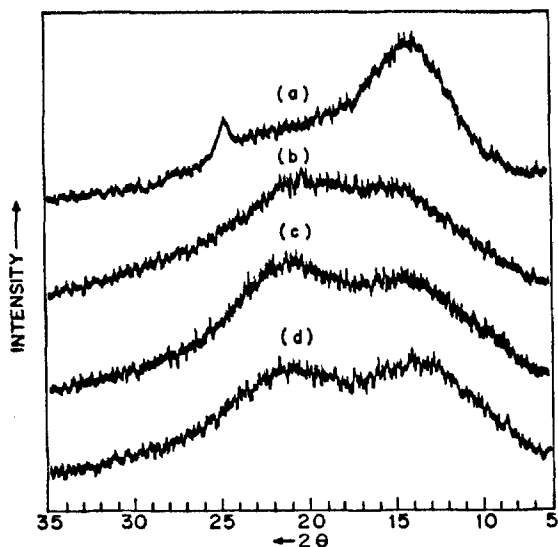


FIGURE 3 X-RAY DIFFRACTION PATTERNS OF PPO(a), PPO MODIFIED WITH PHENYL ISOCYANATE(b), PPO MODIFIED WITH BUTYL ISOCYANATE(c) AND PPO MODIFIED WITH PROPYL ISOCYANATE (d)

Powder X-ray diffraction studies (Figure 3) indicated that the parent PPO exhibits pattern for typical semicrystalline polymer. On the other hand, PPO-AM polymers showed the pattern typical of amorphous materials.

Conclusion

The chemical modification of PPO has been successfully carried out by incorporation of amide groups on PPO aromatic units by electrophilic substitution reaction with aromatic and aliphatic isocyanates. The isocyanate modified PPO polymers are soluble in a broad range of solvents.

References

1.    Bopp, R.C., Gaur, U, Kambour, R.P. and Wunderlich B., J. Therm. Anal., 25(2), 243 (1982).

2.    Jauhiainen, T.P., Angew. Makromol. Chem., 104, 117 (1982).

3.  Cabasso, I, Jagur-Grodzinski, J. and Vofsi, D., J. Appl. Polym. Sci., 18, 1969 (1974).

4.  Chander, K., Anand, R.C., and Varma, I.K., Angew. Makromol. Chem., 127, 137 (1984).

5.  Percec, V., and Auman, B.C., Makromol. Chem., 185(11), 2319 (1984).

6.  Chalk, A.J., and Hay, A.S., J. Polym. Sci., A1(7), 691 (1969).

7.  Xie, S., Macknight, W.J. and Karasz, F.E., J. Appl. Polym. Sci., 29(8), 2679 (1984).

8.  Percec, S.,J. Appl. Polym. Sci., 33(1), 191 (1987).

9.  Hay, A.S., in Macromolecular Synthesis, Collective Volume 1, ed. by J.A. Moore, Wiley 81 (1977).

10. Challis, B.C., Challis, J.A., Compr. Org. Chem., (2), 972 (1979).