International Journal of Engineering Research and Development
ISSN: 2278-067X, Volume 1, Issue 10 (June 2012), PP.80-83
www.ijerd.com

Spectroscopic Estimations of Composition of Engineered Polyphenylene Oxide Copolymers

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Abstract—*Homopolymers of the monomers, 2,6-dimethyl-phenol (DMP) and 2,6-diphenyl-phenol (DPP) and their engineered copolymers were synthesized in the respective initial molar ratio of (i) 90:10 (Co-A), (ii) 75:25 (Co-B), and (iii) 65:35 (Co-C). Dense films of all these synthesised polyphenylene oxide polymers were prepared by the complete solvent evaporation of their chloroform solutions. The films were characterised by FTIR and Proton NMR spectra for determining the copolymer composition by quantitative estimations. The results indicate that the values obtained from FTIR measurements are more reliable for the copolymers having low contents of DPP. Furthermore, the values obtained from FTIR and NMR calculations indicate that the final copolymer formed has a lower compositional value compared to the initial monomer ratio taken. The polymers were also characterised by dynamic mechanical thermal analyser (DMTA) for glass transition temperature (T_g) values which strongly correlated with the calculated copolymer compositions.*

Keywords—*Polyphenylene Oxide; Copolymer Composition; FTIR; NMR; Glass Transition Temperature*

I. INTRODUCTION

Membrane separation of small and similar sized low molecular weight olefin and paraffin mixtures is an emerging interdisciplinary area of research which awaits its much wider acceptance in industry. It critically requires selection of those materials which not only produce good separation characteristics, but also are cost effective and resistant to the stringent industrial conditions such as high thermal and hydrolytic instabilities. Recent developments in membranes separation technology although produce excellent separations, their higher production costs encourage polymer based membranes as potentially promising in many aspects. Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) can be listed as one such engineering polymers due to its high thermal stability (high glass transition temperature (T_g =210°C), high mechanical strength, and excellent hydrolytic stability [1]. In addition, its distinctive but simple structure allows a variety of modifications in both aryl and benzyl positions: (1) electrophilic substitution on the benzene ring of PPO [2], (2) radical substitution of the hydrogen from the methyl groups of PPO [3], (3) nucleophilic substitution of the bromomethylated PPO (BPPO) [4], (4) capping and coupling of the terminal hydroxyl groups in PPO chains, [5] and (5) metalation of PPO with organometallic compounds [6]. These modifications can fine tune PPO for preparation of membranes with specific properties for specific application.

Formation of copolymers of the phenylene oxide family by coupling of terminal hydroxyl groups of dimethyl phenol and diphenyl phenol is an effective method of engineering polymer properties, namely, the thermal and oxidation resistance in the present case. In this short communication, we report the simple spectral determination of the copolymer composition of the various copolymers of polypheylene oxide synthesised. Homopolymers and copolymers of the DMP and DPP monomers were synthesised starting with various initial monomer ratios. Dense films were cast from their chloroform solutions at ambient conditions by solvent evaporation. These polymer films were characterised by FTIR and proton NMR spectroscopy and their glass transition temperature (T_g) was obtained by DMTA. The spectral data was utilised to calculate the copolymer composition of the various polymers synthesised.

II. EXPERIMENTAL

Monomers, 2, 6-Dimethyl-phenol (DMP) and Dibutyl-amine (DBA) were procured from Merck Chemie, Mumbai; monomer 2, 6-Diphenyl-phenol (DPP) was obtained from Aldrich Chem Co., Cuprous bromide catalyst from Lancaster and synthesis grade toluene and chloroform from Ranbaxy were procured. Distilled methanol was used for washing the polymer precipitate.

A. Synthesis of the PPO polymer and copolymers with DPP

The synthesis of PPO from its DMP monomer was carried out according to the procedure given in literature [7]. Copolymers of DMP and DPP with the initial monomer molar ratio of 90:10, 75:25 and 65:35 were also prepared in the same manner.

B. Polymer Characterization

1) FTIR analysis: Fourier Transform Infrared Spectroscopy (FTIR) was performed on the chloroform cast thin films (30 micron thick) of the synthesized polymers. Shimadzu FTIR instrument was used for scanning the films, at ambient temperature, at the rate of 400 sweeps per sec.

2) Proton NMR: Gemini 200 MHz machine was used to determine the structure of the synthesized copolymers and the homopolymer (solvent $CDCl_3$)

3) DMTA: Dynamic mechanical thermal analyzer DMTA model IV, Rheometric Scientific, USA, was used to find the T_g of the polymers from the temperature corresponding to the maximum tan δ value. The temperature range of 25 – 350°C was scanned at the rate of 5 °C per minute and a strain rate of 0.75% at a frequency of 1.5 Hz, in compression mode. Discs of 16mm diameter were prepared from the samples of the measurement. The T_g reported in this paper corresponds to maximum of tan δ values of the samples.

III. RESULTS AND DISCUSSION

The FTIR and proton NMR spectra of all the synthesised homopolymers and copolymers of polyphenylene oxide are elaborated as follows:

A. FTIR

Fig. 1 shows FTIR spectra of the PPO and copolymers Co-A, Co-B and Co-C synthesised.

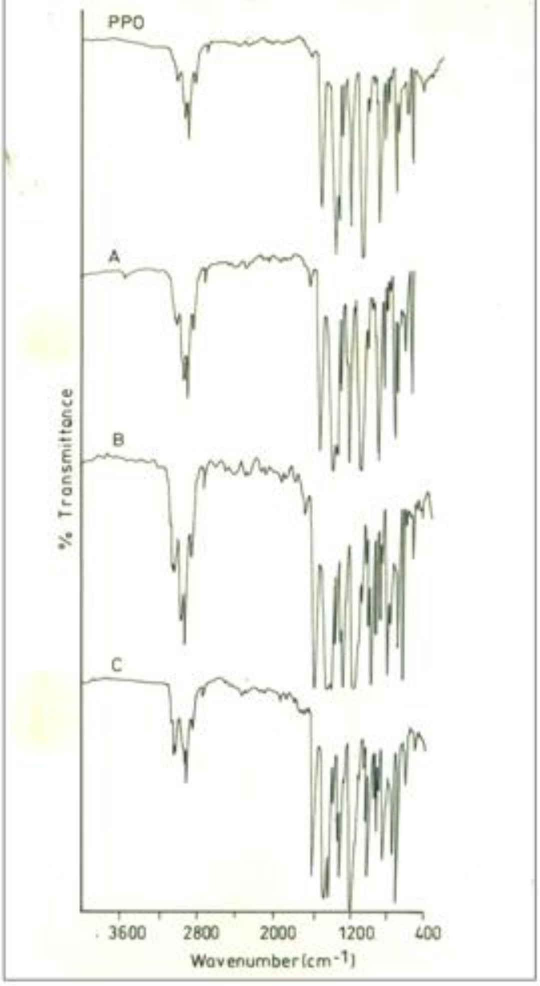

Fig. 1 FTIR spectra of PPO and its copolymers (A) Co-A, (B) Co-B and (C) Co-C

1) PPO: The characteristic aromatic ring –C-H stretching bands occur at 3036 cm^{-1} and 2954 cm^{-1}. 1306 cm^{-1} and 1022 cm^{-1} are the C-O-C (ether) group stretching vibrations and their characteristic deformations occur at 1185 cm^{-1} – 1200 cm^{-1}.

2) Co-polymers: The FTIR Spectra of the copolymers are very much similar to that of the PPO, except for the presence of extra bands characteristic of 2,6-diphenyl group substitutions. Aromatic C-H asymmetric stretching band at 3036 cm^{-1} was found proportionately resolved further into two distinct peaks as 3055 cm^{-1} and 3036 cm^{-1} with the increasing concentration of the 2, 6-diphenyl groups. These peaks indicate the separate and distinct presence of substituted phenyls and back-bone phenyl groups respectively.

B. Proton NMR spectra of PPO and Copolymers

Fig. 2 represents proton NMR of PPO and copolymer Co-A. Due to its simple structure PPO exhibits a six proton singlet corresponding to the two equivalent methyl protons which is observed at tan δ = 2.1 ppm and the remaining two equivalent aromatic protons give two proton singlet at tan δ = 6.4 ppm.

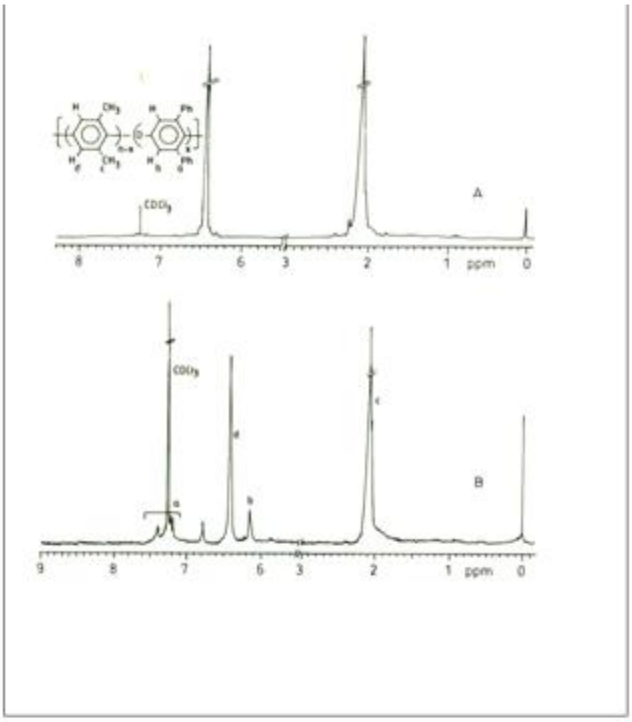

Fig. 2 Proton NMR of (A) PPO and (B) Co-A

In the case of copolymers, there are two sets of equivalent protons existing in two different chemical environments. At tan δ = 2.0 - 2.2 ppm (singlet –CH3 protons labelled 'c'), at tan δ = 6.150 ppm (Ar-H labelled 'b'), at tan δ = 6.43 ppm (singlet Ar-H labelled 'd') and at tan δ = 6.7 – 7.5 ppm (multiplet aromatic protons labelled 'a') are observed.

C. Calculation of Copolymer Ratio

FTIR spectra helps in quantitatively evaluating the exact composition of the final copolymer formed [8]. FTIR and proton NMR spectra of the synthesised copolymer samples were used to determine the copolymer composition. Table 1 shows the copolymer composition which is expressed in terms of mol% of DPP content present in the synthesized copolymers.

The IR absorption in the region 2860-3100 cm^{-1} is due to methyl hydrogen atoms and aromatic C-H of the polymer. Mixtures of homopolymers of DMP and DPP were prepared in respective mole ratio from 100:0 to 50:50 in chloroform and cast as films. FTIR spectra of these vacuum dried films of 30 micron thickness were recorded. Ratio of the area of peaks under 2860 – 3100 cm^{-1} and 1200 cm^{-1} versus mol% of DPP was utilized to estimate composition of the copolymer by interpolation.

TABLE 1: COPOLYMER COMPOSITION (CALCULATED AS DPP MOL %) DETERMINED BY QUANTITATIVE FTIR AND PROTON NMR ANALYSIS

Polymer	**T_g (°C)**	**Initial monomer ratio (mol%)**		**Calculated comonomer (DPP) concentration (mol %)**				
		DMP	**DPP**	**IR^{+}**	**NMR***			
					δ(6.15/2)	**δ(6.43 /6.15)**	**Average**	**Wt %**
Co-A	235	90	10	6.25	9.08	8.58	8.83	15.1
Co-B	262	75	25	13.20	15.17	13.89	14.53	25.8
Co-C	299	65	35	-	25.80	21.50	23.68	38.2

$^{+}$ *Values reported for DPP mol% calculated by IR is within error margin <0.5%*

* *Values reported for DPP mol% calculated by NMR is within error margin < 0.3%*

Upto a DPP content of 20 mol% a straight line fit helped in finding copolymer composition. Beyond 20 mol% of DPP content, scattered points indicated poor relation between monomer and copolymer proportions hence composition could not be estimated for copolymer Co-C from IR measurements.

The comonomer content (mol%) was also calculated from the proton NMR spectra of the copolymer samples by calculating the ratio of peaks at tan δ =6.150 ppm vs peak at tan δ =2.0 – 2.2 ppm and the ratio of peaks at tan δ= 6.430 versus peaks at tan δ =6.15 ppm.

The results indicate that the values obtained from FTIR measurements are more reliable for the copolymers having low contents of DPP. Furthermore, the values of comonomer content obtained from IR and NMR calculations indicate that the final copolymer formed has a lower compositional value compared to the initial monomer ratio taken. This can be due to the differences in the reactivity of DMP and DPP.

D. DMTA

Table 1 gives the values of Tg obtained from DMTA measurements. The T_g for PPO was found to be 235 °C. Co-A exhibited a T_g of 234.96 °C, almost similar to that of PPO. This probably implies that incorporation of 8 mol % of DPP units in Co-A could not produce significant effect on changing the segmental mobility (flexibility) of the polymer chains. However, beyond 8 mol%, the T_g values increased significantly with the further increase in the content of DPP. This implies that beyond 8 mol% the effect of DPP content on increasing the polymer chain rigidity is pronounced. Probably, the presence of higher proportions of rigid phenyl groups of DPP reduce the segmental mobility of the polymer chains, when compared to PPO and Co-A.

A correlation graph (Fig. 3) plotted between the calculated DPP mol% for the various copolymers versus their T_g values presented a least square straight-line fit with a strong correlation (R^2=0.999). The correlation also supports the calculated values of copolymer composition.

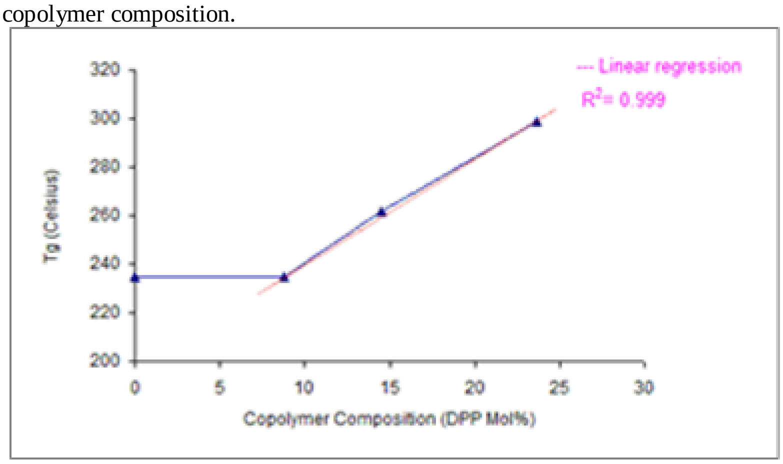

Fig. 3. Glass Transition Temperature vs Copolymer Composition

IV. CONCLUSIONS

The determination of the composition of the copolymers of DMP and DPP is carried out using quantitative analysis of FTIR and proton NMR spectra. The results indicate that the final copolymer formed has a lower compositional value compared to the initial monomer ratio taken. These copolymers based membranes have exhibited promising potential in the separation and recovery of useful hydrocarbons from mixtures [9].

V. NOMENCLATURE

PPO : Poly(2,6-dimethyl-1, 4-phenylene oxide)
Co-A : Copolymer-A with initial DMP:DPP molar ratio 90:10
Co-B : Copolymer-B with initial DMP:DPP molar ratio 75:25
Co-C : Copolymer-C with initial DMP:DPP molar ratio 65:35
Error % : (Standard deviation of values/Arithmetic mean of values) x 100
R^2 : Correlation Coefficient of Linear regression (Least square fit)

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