Aromatic Polyesters Based on Bisphenol-A for Liquid Insulating Systems: A Synthetic Approach

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ABSTRACT: This work concentrates on the area of the synthesis of polymers for liquid insulating systems. We have studied reactions of aromatic esters like diphenyl terephthalate/isophthalate, diphenyl carbonate with Bisphenol-A, and tri functional glycerol for the synthesis of aromatic polyesters that can be used as liquid insulating systems. The process comprises a transesterification resin synthesis based on a single pot process, with a temperature profile up to 250°C and an inert atmosphere of nitrogen. The byproduct of the phenol is continuously removed under a steady flow of nitrogen to enable polycondensation. The resins obtained were tested for their physical properties, such as melting range, relative viscosity, and hydroxyl value. These resins were also used in solution film formation to establish their film forming properties. The method explored is the simplest one, and permits the use of commercial materials as the feedstock. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 95: 606–614, 2005

Key words: polyesters; polycondensation; films; synthesis; infrared spectroscopy

INTRODUCTION

There are three major processes described in the literature for the preparation of aromatic polyesters. These are: (a) an interfacial polycondensation of terephthaloyl chloride/isophthaloyl chloride (TPC/IPC) with Bisphenol-A (BPA) under phase transfer conditions, (b) melt polycondensation of BPA-diacetate with terephthalic acid/isophthalic acid (TPA/IPA) in the presence of a catalyst, and (c) melt polycondensation of diphenyl terephthalate/diphenyl isophthalate (DPT/DPIT) with BPA in the presence of a catalyst.[1] Literature does not show any elaborate method for the synthesis of aromatic polyesters for liquid insulating systems, and a relation to the structure of these resins and their functional contribution to the properties has long been eluded.

In view of this, the present study was undertaken to prepare a flexible insulation for wires and develop a resin with an aromatic backbone that could be easily produced through the use of various raw materials available indigenously at a more economical cost. As is known, polycarbonate from BPA possesses excellent electrical and mechanical properties. A modification of this polymer could be arrived at where an insulation, having all the requisite properties, could be produced at a more economical cost. Thus, use of DPT, DPIT, BPA, diphenyl carbonate (DPC), and glycerol were used for this investigation. A further study on the molecular structure and arrangement of functional groups in the resin was also made by the use of infrared spectroscopy (IR) and nuclear magnetic resonance spectroscopy (NMR) to predict a probable structure for the resin synthesized and the properties obtained from the final insulating system. The process is attractive as it permits the use of readily available starting materials. The byproduct of the reaction is phenol, which is eliminated by distillation and a steady stream of nitrogen.

EXPERIMENTAL PROCEDURES

Physical properties

Melting range, hydroxyl value, and viscosity of the resin samples were carried out as per standard procedures mentioned for resins for insulating systems.[2]

Substrate

To correlate the properties of the resin and the film obtained, it was decided to carry out the studies on aluminum panels of the size of 10 cms × 10 cms and about 1mm in thickness. The surface of the aluminum panel was made free from grease, preheated, and cleaned with dilute acid solution and further ensured

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clean by rubbing it with cotton wool dipped in benzene.

Resin solution preparation

A solution of 35% solids of resin in a solvent combination comprising of Phenol: 45% (w/w), Cresol: 15% (w/w), and C9: 40% (w/w) was prepared. The solutions were warmed to about 80°C (±5) so as to ensure complete solubility of the resin, and filtered to remove any unwanted suspended particles. These filtered solutions were then cooled to room temperature, and to this solution was added butyl titanate monomer as crosslinker: 4% (w/w) on quantity of resin. The solutions were properly stirred to obtain a completely homogeneous solution. These solutions were then poured over the panels to obtain a film of the resin. The films cast on the aluminum panels by the flow method were baked at the specified temperatures, so as to ensure complete evaporation of the phenolic solvents.

Standardized oven temperatures for curing schedule

First coat: 140°C for 1 h and 180°C for 2 h.

Second Coat: 140°C for 1 h and 180°C for 2 h.

The resultant film thickness was about 55–60 microns.

Mechanical properties

Adhesion, flexibility, and hardness of the insulating film on the aluminum panel were tested according to IS standards.[2]

Infrared spectroscopy (FTIR)

Infrared studies (FTIR) of the resins synthesized were recorded on a Shimadzu FTIR–4200 as pellets in potassium bromide.

Nuclear magnetic resonance (NMR)

Spectra (δ, ppm) were scanned on a Varian Gemini-2000 (200 MHz) spectrophotometer using TMS as the internal standard.

Gel permeation chromatography (GPC)

The GPC for the synthesized resin was done by dissolving the resin in Tetra hydro furan solvent (0.05%). The column was of a mixed porosity and standardized against polystyrene as a reference standard. The temperature was 35°C, with a flow rate of 1 mL/min. A refractive index detector was used for detection of eluted solution.

Materials

Bisphenol-A (BPA): analytical grade BPA of m.p. 158–159°C was procured from M/s S.D. Fine Chemicals Ltd. Glycerol: reagent grade, purity was found to be 96%, R.I. 1.5630*M*/s S.D. Fine Chemicals Ltd. DPC: synthesis grade DPC with m.p. 79–80°C, imported from MERCK, Germany. TPA: TPA was supplied by M/s Reliance Industries Ltd., m.p. 305°C. IPA: IPA was supplied by M/s Reliance Industries Ltd., m.p. 305°C. Thionyl chloride: reagent grade thionyl chloride of bp 110°C was obtained from a local supplier.

TABLE I
Resin compositions and resultant properties for Resins PE 1–4

Test/Resin	PE-1	PE-2	PE-3	PE-4
Composition	BPA-2 DPT-0.8 DPIT-1.2	BPA-2 DPT-1 DPIT-1 DPC-1	BPA-1 DPC-1 DPIT-1 — GLY-1	BPA-2 DPC-1 DPT-1 DPIT-1 GLY-1
% Aromatic	69.59	69.83	62.44	65.23
% Aliphatic	8	6.4	9.74	8.94
% Ester	16.1	13.4	10.32	12.58
% Carbonate	—	4.59	7	4.29
% Hydroxyl	6.2	2.6	9.97	6
A : B	4A : 4B	6A : 4B	4A : 5B	6A : 7B
Hydroxyl value*	40–45	55	165–170	175–180
Melting Range °C	115–140	140–200	85–90	95–105
Relative Viscosity	1.08	1.43	1.12	1.104
GPC				
Mw	4843	48336	25985	14350
Pd	1.952	9.73	5.39	9.53
Adhesion	Fails	Fails	Excellent	V.good
Flexibility	Fails	Fails	Pass	Pass
Pencil hardness	Fails	Fails	Excellent	Excellent

*mg of KOH/gm of resin.

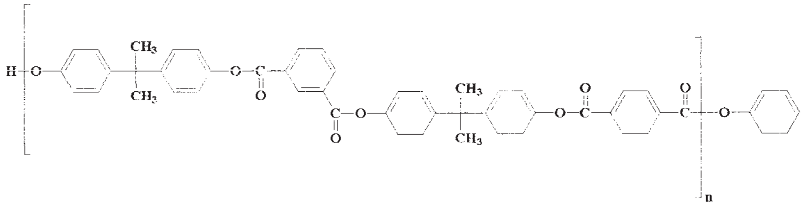

Figure 1 Probable structure of resin containing BPA, DPIT, and DPT (PE-1).

Potassium hydroxide: reagent grade was obtained from a local supplier. Irganox B-561: procured from M/s Ciba Speciality Chemicals Ltd. Antimony trioxide: procured from M/s S.D. Fine Chemicals Ltd.

General chemicals

Mineral acids and organic solvents such as 1,1,2,2-tetra-chloroethane, xylene, methanol, benzene, *m*-cresol, and phenol, were of technical grade and were distilled before use.

Synthesis of the aromatic phenyl esters

Synthesis of DPIT[3] and DPT[4]

Synthesis of DPIT was done by phase transfer reaction from IPA and TPA, respectively, according to Zhang. The melting point obtained for DPIT was 138°C (lit. 135–137°C) and DPT was 198°C (lit. 197°C).

Synthesis of the resins

Calculations

Each composition synthesized using the different raw materials was carried out based on the mole proportions required to obtain an acid or a base terminated resin. The percentage of aromatic, aliphatic, ester, carbonate, and hydroxyl content present in the composition was theoretically calculated considering elimination of the phenol byproduct and assuming a repeating unit structure. In these compositions, the ester is considered as an acidic component.

Polyester of BPA, DPT, and DPIT[4] (PE-1)

Transesterification of BPA, DPIT, and DPT was carried out as follows: 23.89g (0.104 mol) BPA, 13.33 g (0.041 mol) DPT, 20.0 g (0.062 mol) DPIT, and 0.016 g (0.022% on charge) antimony trioxide were placed in a 3-necked round bottom flask equipped with a nitrogen inlet, a thermometer pocket, a side arm for distillation, and a 2-loop stirrer for mechanical agitation. The temperature was raised to 180°C and maintained at this temperature until the oligomerisation of BPA took place. This was checked by thin layer chromatography using silica gel as a stationary phase and benzene : toluene (70 : 30) as a mobile phase. 0.026 g (0.05%) Irganox was added at 190°C and was stirred into the solution for half an hour. The temperature was then raised stepwise at intervals of 10°C per hour to 220°C. At this time phenol distilled out and an increase in viscosity of the solution was observed. Once phenol distillation ceased, the temperature was again raised stepwise to 240°C. The polycondensation was continued until a tack free resin was obtained. The resin was poured onto an aluminum tray and allowed to cool. Resin was brown in color and transparent. It was characterized for its physical properties as shown in Table I and Figure 1.

Incorporation of carbonic acid by use of DPC and its effect on the resin structure and properties (PE-2)

Using DPC makes the resin a carbonate ester. Thus, 45.6g (0.2 mol) BPA, 31.8g (0.1 mol) DPT, 31.8g (0.1 mol) DPIT, and 21.4g (0.1 mol) DPC with 0.30g (0.2% on charge) antimony trioxide and 0.05g (0.07% on charge) Irganox were reacted under experimental conditions of PE-1. A vacuum of 100–150 mm of Hg was

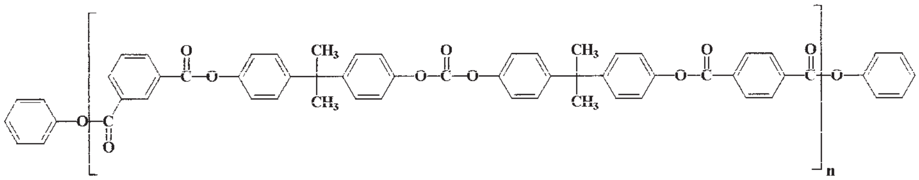

Figure 2 Probable structure of resin containing BPA, DPIT, DPT, and DPC (PE-2).

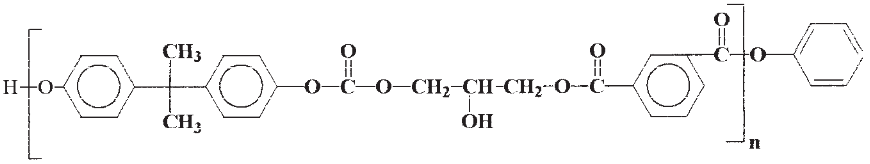

Figure 3 Probable structure of resin containing BPA, DPIT, glycerol, and DPC (PE-3).

applied for one hour. The resin was characterized for its physical properties as shown in Table I and Figure 2.

Modification of PE-1 by incorporation of glycerol and replacing one acidic component in the system (PE-3)

A trifunctional moiety like glycerol can increase the hydroxyl content as well as provide a functional group for some degree of crosslinking. Use of one phenyl terephthalate like DPIT was thought worthwhile to balance the acid to base ratio in the resin. Thus, 31.96g (0.140 mol) BPA, 44.57 g (0.140 mol) DPIT, 30.04 g (0.14 mol) DPC, and 12.89g (0.140 mol) glycerol with 0.085g (0.05% on charge) lithium hydroxide and 0.0085g (0.005% on charge) Irganox were reacted under experimental conditions of PE-1. The resin was characterized for its physical properties as shown in Table I and Figure 3.

Modification of PE-2 by glycerol (PE-4)

Modification of PE-2 was carried out using glycerol as a trifunctional component. Thus, 51.5g (0.22 mol) BPA, 25.7g (0.11 mol) DPT, 25.7g (0.11 mol) DPIT, 21.4g (0.1 mol) DPC, and 10.34g (0.11 mol) glycerol with 0.026g (0.2% on charge) lithium hydroxide and 0.06 g (0.005% on charge) Irganox were reacted under experimental conditions of PE-1. The resin was characterized for its physical properties as shown in Table I and Figure 4.

DISCUSSION

The aim of the present investigation, as mentioned earlier, was to synthesize resins as film forming compositions to be used in formulating insulating enamels and impregnating varnishes. Our study has been mainly confined to liquid insulating systems.

The process used for the synthesis of the resins was the melt fusion process. It was thought to be the most effective process so as to maintain a uniform homogeneity as well as provide efficient temperature control in the system. Temperatures used for synthesis of the resins were of the order of 240–260°C. Temperature above 260°C was not used due to decomposition and oxidation of the product, as well as auto oxidation of BPA. A vacuum ranging from 100 to 150 mm Hg was used to initiate polymerization at temperatures in the range of 200–220°C. The byproduct of the reaction, phenol was continuously removed by the passage of a fast flow of nitrogen gas, thus also maintaining inert atmospheres.

To gain an increase in the thermal stability, the presence of aromatic groups in the resin structure plays a vital role. With this in mind, formulations based on BPA coupled with materials like DPT, DPIT, DPC, and glycerol were used in various stoichiometries to yield various resin compositions. The probable structures for the respective polyesters are proposed.

Analysis of the resins by FTIR, NMR spectroscopy

The IR (Figs. 5a–d) and ^{1}H-NMR (Figs. 6a–d) spectra for the resins synthesized are presented, respectively. A variation of the carbonyl stretching of the aliphatic ester from 1730–1740 cm^{-1} (Figs. 5a–d) is attributed to the progressive formation of aromatic polyester. This band is typical of an aromatic structure.[5] There is also an important relative reduction in the intensity of the –OH band at 3500 cm^{-1} in the Figures. This is quite obvious because of the fact that the end group –OH concentration in the high molecular weight polyester will be totally negligible. The overall IR spectra of the final polyesters are identical with the IR spectrum of the authentic polyester sample obtained by interfacial polymerization.[6]

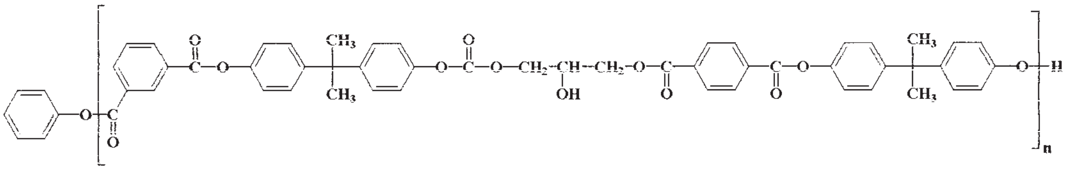

Figure 4 Probable structure of resin containing BPA, DPIT, DPT, glycerol, and DPC (PE-4).

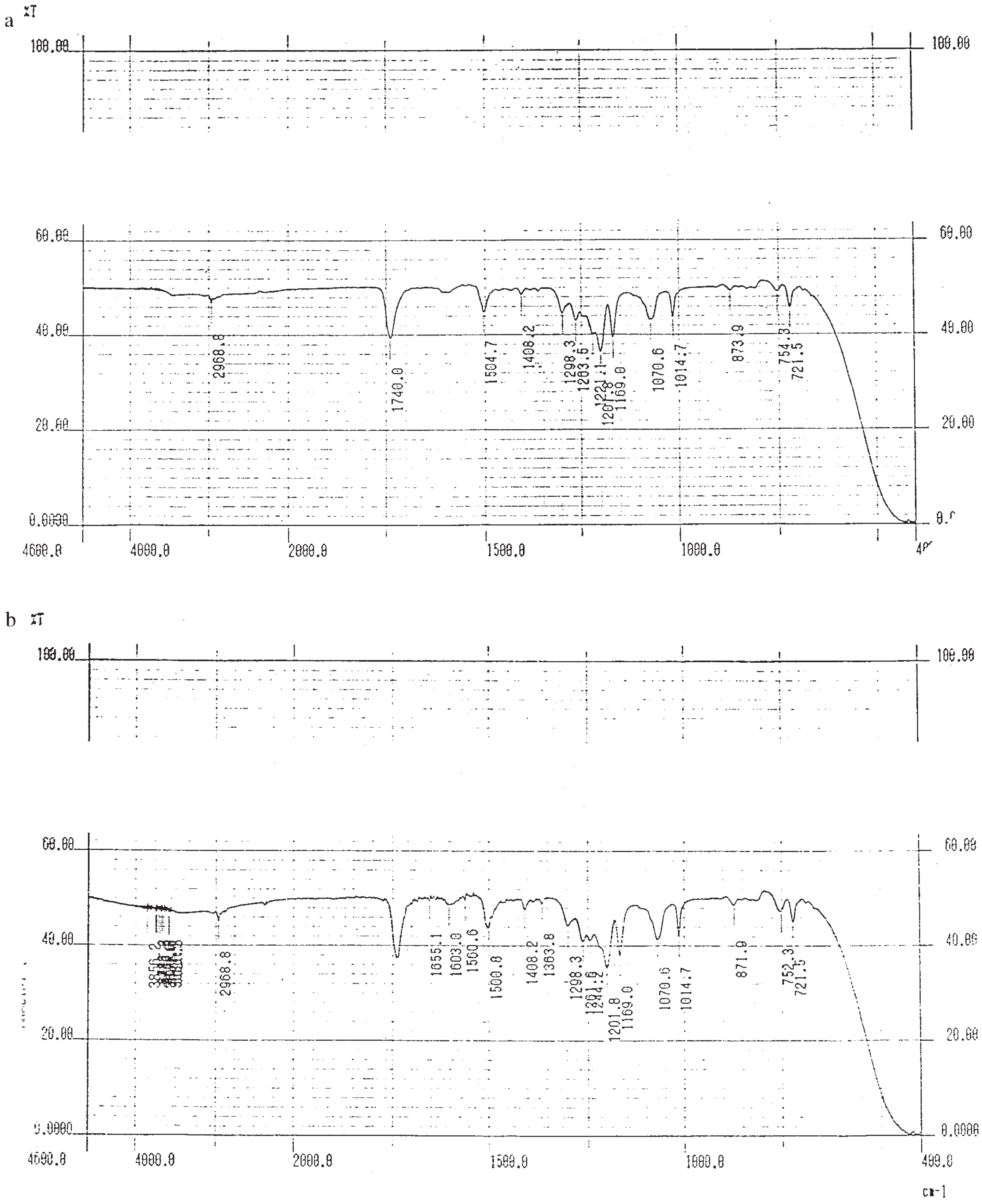

Figure 5 Infrared scans of resins PE 1–4.

The proton NMR analysis of the samples is of great interest because important information concerning the structure of the resins can be obtained from it. In the region between 8 and 8.4 ppm, typical of a terephthalic unit, the NMR spectrum of the resins (Figs. 6a,b) shows four additional peaks between 8 and 8.35 ppm, in addition to the singlet at 8.4 ppm due to the symmetrical aromatic ester, a substituted terephthalate unit. The additional peaks between 8 and 8.35 ppm show a pattern of para disubstituted benzene, having dissimilar ester groups. The upfield doublet centered at 8.2 ppm is because of the aromatic protons, ortho to end methyl ester group, as expected, and the other doublet centered at 8.3 ppm is because of the aromatic

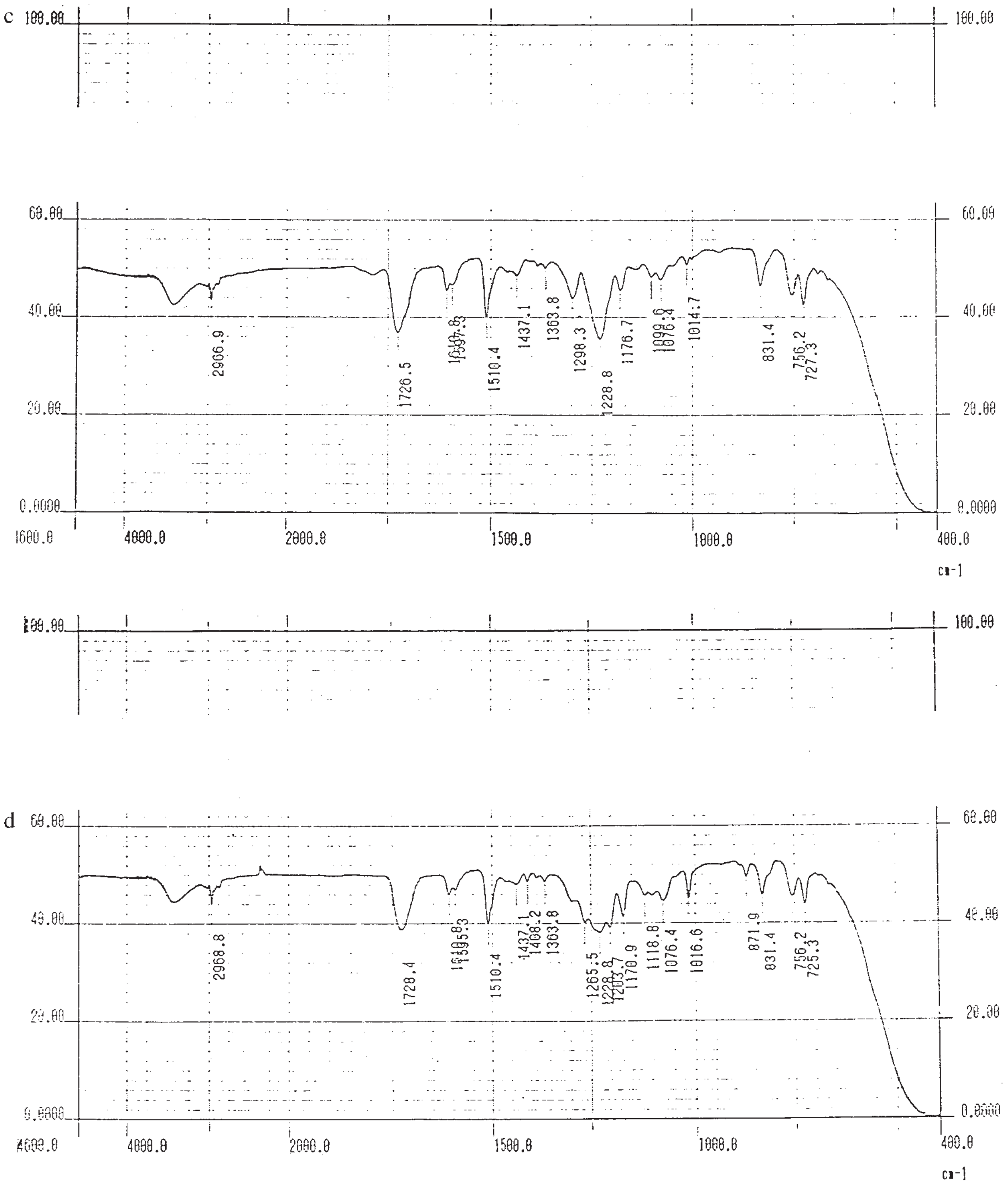

Figure 5 (*Continued*)

protons, ortho to aromatic ester moiety. Similar observations have been reported by Gouinlock et al.[7] while studying BPA–neopentyl glycol terephthalic acid co polyester.

The symmetrical aromatic ester substituted isophthalic unit shows proton shifts at 9.05, 8.5, and 7.7 ppm. However, the proton region of the isophthalic unit also shows additional peaks at 8.9, 8.4, and 7.6 ppm. These upfield shifts observed for all three protons for the isophthalic unit can be attributed to the end phenyl ester of the isophthalic unit. The analysis of this part of the spectrum clearly shows that the resins contain terephthalic/isophthalic units having a phenyl ester end group in addition to terephthalic/isophthalic units, substituted by aromatic ester groups.

The symmetrical aromatic ester substituted BPA moiety shows aromatic proton shifts in the region of 7–7.5 ppm, with the aliphatic protons singlet at 1.6

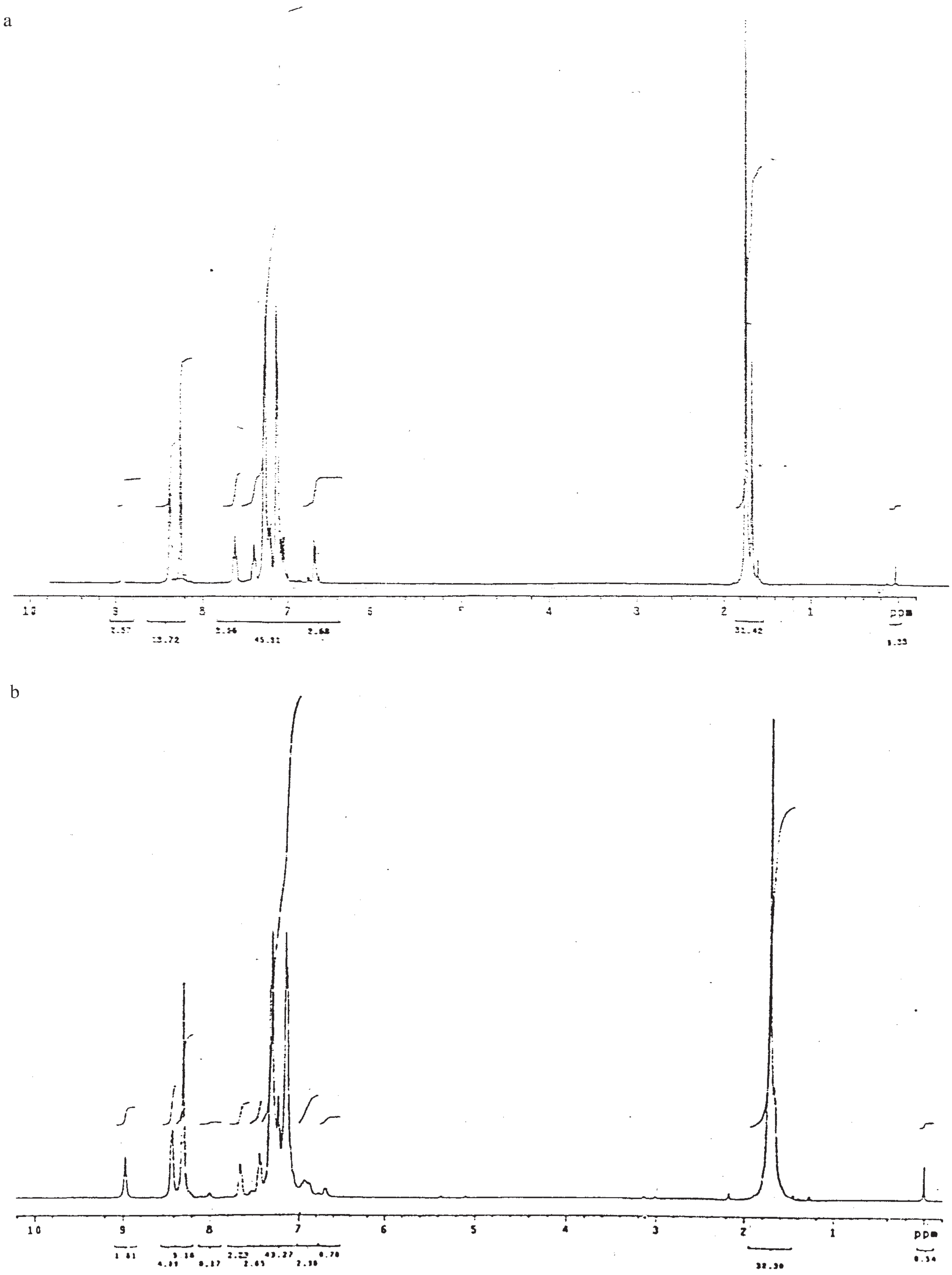

Figure 6 NMR scans of resins PE 1–4.

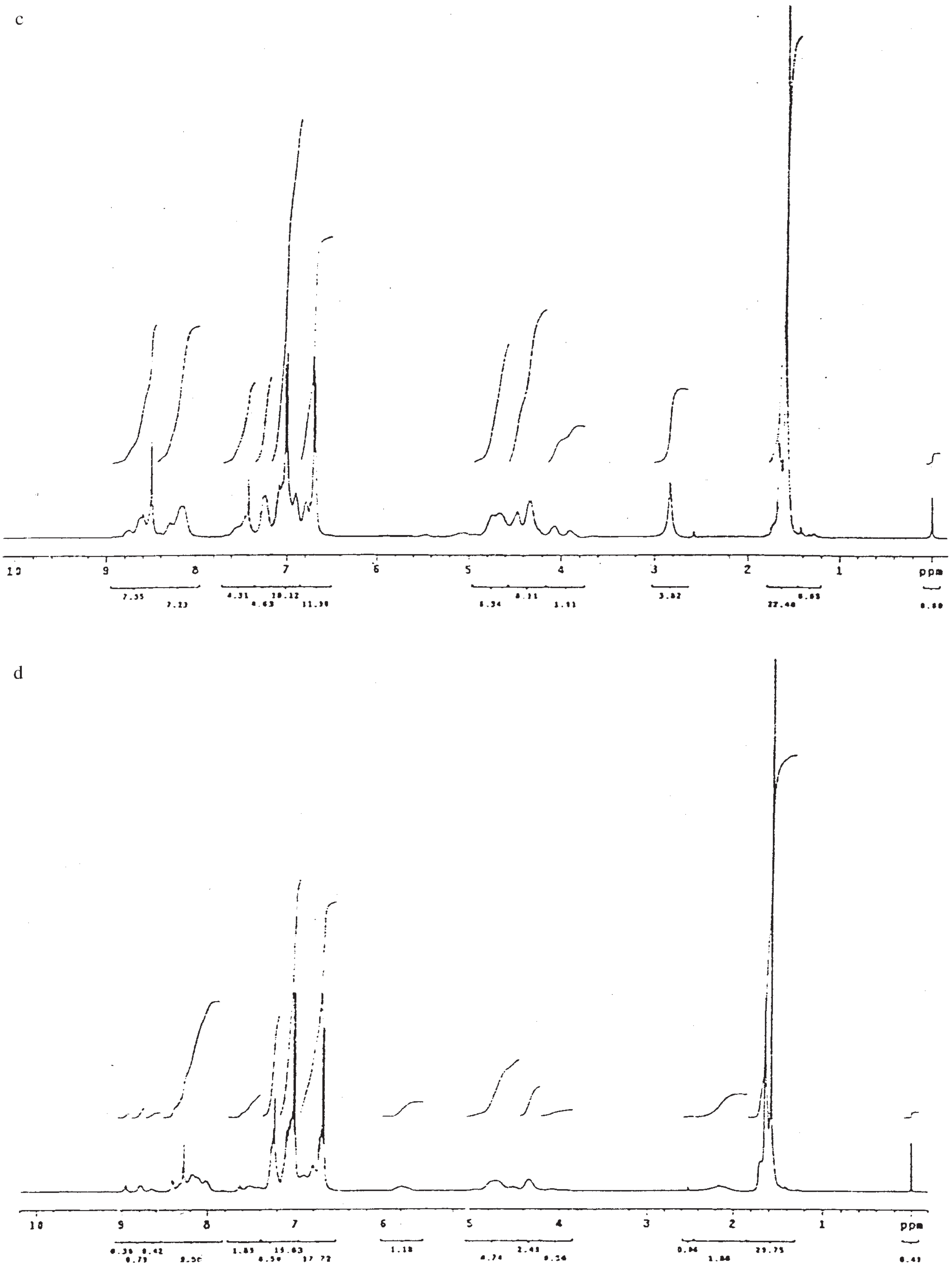

Figure 6 (*Continued*)

ppm. In addition to these shifts, additional peaks are observed at higher fields in both the regions. It is well known that the Phenolic –OH group is a strong electron donor and exhibits a shielding effect on ortho, meta, and para protons of the aromatic nucleus, causing upfield shifts.

The upfield doublet centered at 6.75 ppm (Fig. 6b) is due to aromatic protons ortho to the end –OH group of BPA moiety. The upfield shift in the aliphatic region is due to the modification in the surrounding of methyl groups in the BPA moiety having the –OH end group.

The ^{1}H-NMR spectrum of the resin PE-1 (Fig. 6a) is identical with the ^{1}H-NMR spectrum of an authentic sample of aromatic polyester obtained from BPA, terephthaloyl/isophthaloyl chloride by interfacial polymerization.[7]

The aliphatic protons of the glycerol unit occur as multiplets in the region of 3.5–5.5 ppm. (Figs. 6c,d) It was not possible to pinpoint particular peak shifts for each individual proton for these aliphatic protons. Based on these shifts, the probable structures for the resins synthesized are presented.

Gel permeation chromatography of resins (GPC)

The one pot synthesis sequence followed does not enable a graded determination of molecular weight. As seen, PE-1 with an equimolar stoichiometry exhibits a polydispersity (Pd) of 1.9 and a low molecular weight. Analogous to this, PE-2–4 show a high Pd and a corresponding high molecular weight and a correspondingly high Pd. This would be due to the excess of either the basic hydroxyl component or the excess acidic ester component. This theory is also supported by the hydroxyl value.

Mechanical properties of resins

As seen in Table I, PE-1 and 2 fail in all the mechanical properties necessary to form a good film for insulating systems. This could be due to the high aromatic content of 69% with unequal distribution of polar groups due to low aliphatic linkages not giving the polar groups access to the metal surface. PE-3 and 4 show better enhanced mechanical properties, which could be due to the presence of the trifunctional glycerol moiety and hydroxyl groups present, which causes spacing out of the polar ester groups by the propylene linkage for better surface interaction and more molecular mobility. This is very clearly visible in PE-4, which shows a slight lowering of adhesion by a corresponding increase in aromatic content by 4% on the incorporation of an extra mole of BPA.

CONCLUSIONS

A novel synthetic route to synthesize resins for liquid insulating systems using melt fusion techniques and simple materials was achieved. A relative viscosity of 1.08–1.10 was obtained for the resins. A trifunctional moiety like glycerol contributes to better mechanical properties for film forming substances, which also works well for high aromatic content systems.

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