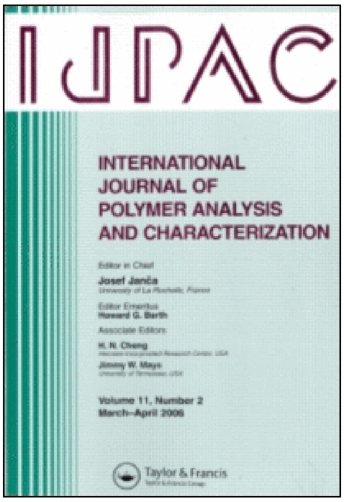

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Synthesis, Characterization, and Properties of Flame-Retardant Polyurethanes

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Abstract: Phosphorous-containing flame-retardant polyurethanes were prepared and characterized by various chemical and instrumental analysis techniques. Various physical and thermal properties of the polymers were established. Flame-retardant characteristics of polymers in the form of film were determined. Polymer films show good resistance towards ultraviolet light and various chemical agents. Polyurethanes possess good flame-retardant and chemical-resistance properties.

Keywords: Limiting oxygen index; Polyurethanes; Properties; Synthesis

INTRODUCTION

Polyurethanes are an important class of polymers used in various applications like furniture, flexible slabs, refrigeration, coatings, adhesive formulations, and in certain military and mining applications.[1,2] In many of these applications, flame-retardant property is in great demand to prevent fire hazards. The versatile applications of polyurethane encourage us to synthesize and characterize the intrinsic type of phosphorous-containing polyurethanes. The presence of phosphorous

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and nitrogen moieties in addition to aromatic ring in the backbone chain structure makes them thermally and chemically stable.[3]

In the present work, the synthesis of different flame-retardant polyurethanes by reacting the monomer tris-(bisphenol-C)monophosphate with various diisocyanates is described. Characterization of the monomer and polyurethanes has been done by chemical analysis and instrumental techniques. Thermal, flame retardance, photoresistance, and chemical stability of the polyurethanes have also been studied.

EXPERIMENTAL SECTION

The reagents bisphenol-C (BC), phosphorous oxychloride ($POCl_3$), toluene diisocyanate (TDI), hexamethylene diisocyanate (HMDI), diphenyl methane diisocyanate (MDI), and isophorone diisocyanate (IPDI) were obtained from Fluka and were used as such without further purification. Technical grade ammonium phosphate, $(NH_4)_2HPO_4$, was crystallized and used for curing study. Solvents such as methyl ethyl ketone (MEK), methanol (MeOH), and dimethyl formamide (DMF) were used after distillation.

The monomer tris-(bisphenol-C)monophosphate[4] (TBCMP) was synthesized by reacting bisphenol-C (3.0 mole) and phosphorous oxychloride (1.0 mole) at a temperature of 120°–130°C for 10 h in the presence of N,N-dimethyl aniline (0.0132 mole). The resultant mass was washed with ether and dissolved in acetone. The monomer was obtained by neutralizing and precipitating in cold water. Pure product was collected after crystallizing from methanol and dried in vacuo before characterization.

The polyurethanes (PU-1, PU-2, PU-3, and PU-4) (Figure 1) were synthesized in two steps. In the first step, pre-polymers were prepared by reacting the monomer TBCMP (1 mole) with various diisocyanates, namely TDI (PP-1), IPDI (PP-2), HMDI (PP-3), and MDI (PP-4) (each of 3.0 moles), in MEK solvent at 55°C with continuous agitation for 2.5 h in nitrogen atmosphere. In the next step, the pre-polymers were further reacted with excess monomer (TBCMP, 3.0 mole) at 70°C for 4.5 h in the same medium to get the corresponding hydroxyl-terminated phosphorous-containing polyurethanes.

The number of hydroxyl groups of the monomer and the polyurethanes was determined by hydroxyl group estimation. Intrinsic viscosity of the soluble polymers was measured using an Ubbelohde suspended level viscometer in DMF solvent. These values are 0.3, 0.24, 0.2, and 0.25 dl/g respectively for the polyurethanes PU-1, PU-2, PU-3, and PU-4. Percentage yields of monomer and polyurethanes are in the range of 70–74%. Elemental analysis was carried out in a Perkin Elmer USA

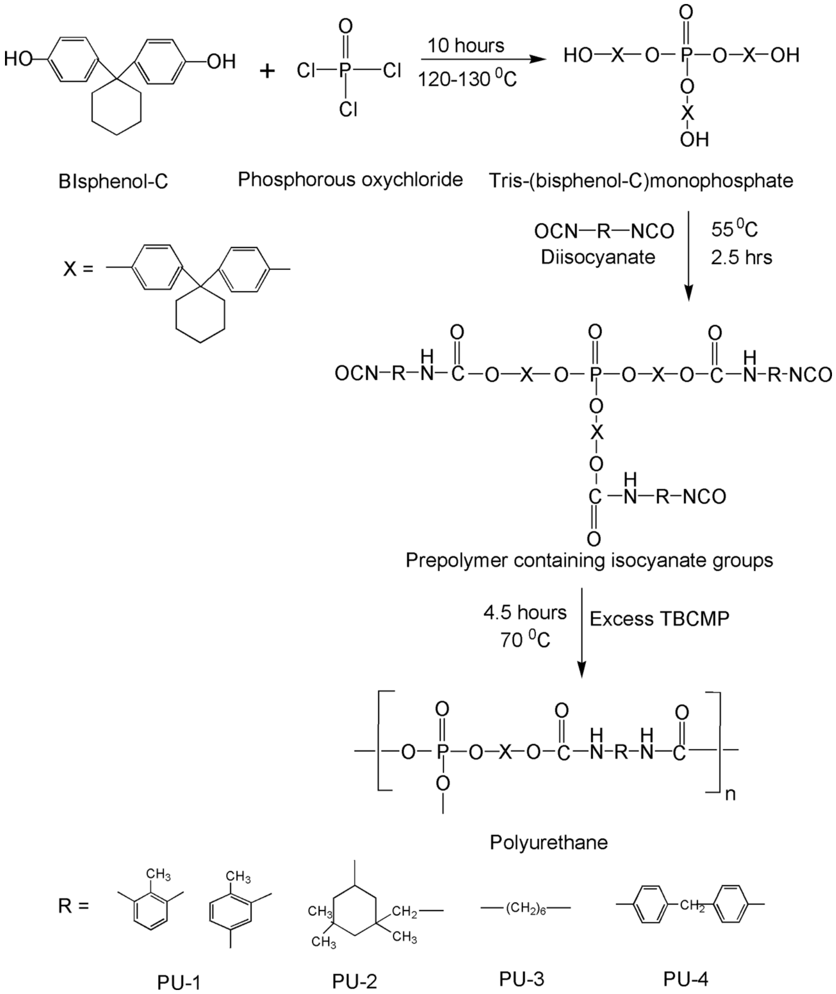

Figure 1. Reaction scheme used for the synthesis of polyurethanes.

model 2400 series II. The infrared spectra of the monomer and polyurethanes were recorded in KBr pellet on a Perkin Elmer USA Spectrum GX Fourier transform-infrared (FT-IR) spectrophotometer. Molecular weight of the polyurethanes was determined by the vapor pressure osmometry technique using a model K-7000 Knauer instrument. Number-average molecular weights of PU-1, PU-2, PU-3, and PU-4 polymers are 3914, 4058, 3896, and 4142 g/mole respectively.

Curing characteristics of the polymers were determined using the differential scanning calorimetry (DSC) technique. Prior to each scan, polyurethane was mixed with the curing agent ammonium phosphate, $(NH_4)_2HPO_4$ (0.1% of total weight of polyurethane sample), and stirred for 3–5 min for proper mixing. The sample was degassed under vacuum. The void-free mixture was used for the DSC scan by taking 4–5 mg of the sample at a heating rate of 10°C/min using empty cell as reference. The heat flow data of the polyurethanes were obtained by DSC using a TA Instrument USA model 5000/2920. Thermogravimetric analysis (TGA) of the polymers was carried out on Perkin Elmer USA TGA-7 thermal analyzer in air at a heating rate of 10°C/min.

Photostability and flame-retardant properties were measured by casting the polyurethane films from a glass mold. Required amounts of phosphorous-containing polyurethane and ammonium phosphate were mixed thoroughly in a suitable solvent and poured on the glass mold. The films were prepared by heating the content at 70°C for 24 h, followed by cooling to room temperature. Stability of the films towards ultraviolet light was determined by using an ultraviolet spectrophotometer, Perkin Elmer model Lambda 19. The limiting oxygen index (LOI) of the films was measured on a standard apparatus as per ASTM standard D 2863.

RESULTS AND DISCUSSION

The elemental analysis reveals that the observed values for the percentage of carbon, hydrogen, and nitrogen of the monomer and all the polyurethanes are in good agreement with the calculated values.

The IR spectrum of the monomer shows a broad absorption band at 3393 cm^{-1} due to the presence of H-bonded hydroxyl species, the band at 1277 cm^{-1} corresponds to Ar-OH symmetric stretching frequency, C=C stretching of aromatic ring is obtained at 1507 cm^{-1}, the band at 1236 cm^{-1} is due to the presence of P=O group, and the band at 993 cm^{-1} is due to the P-O-C stretching frequency.

The IR spectra of polyurethanes show an absorption band around 1595–1643 cm^{-1} for –OCONH asymmetric stretching vibration. The band for P=O group appears around 1224–1237 cm^{-1}. P-O-C stretching frequency is observed around 970–973 cm^{-1}. The broad band around 3250–3345 cm^{-1} is attributed to >N-H bond.

A notable feature is that all the synthesized polyurethanes are stable at room temperature. The curing behavior of the polyurethanes was studied in the presence of 0.1% $(NH_4)_2HPO_4$ using the DSC technique. Table I summarizes the curing characteristics of curing reaction such as the temperature at which curing is initiated (T_i), reaches a maximum (peak) (T_p), and is completed (T_f). Curing parameters, order of the reaction, and activation energy were determined using the

Table I. Thermal and flame-retardant properties of the polyurethanes

	Curing parameters by DSC					% Weight loss from TGA °C				Char yield	LOI
System	T_i°C	T_p°C	T_f°C	n[a]	E[b]	10%	30%	70%	IPDT °C	%	%
PU-1	270	300	330	2.8	195	175	230	575	275	24	34
PU-2	240	250	270	2.6	180	245	290	365	250	22	33
PU-3	270	290	312	2.6	160	225	300	585	285	20	30
PU-4	280	290	300	2.7	162	185	280	—	260	33	36

T_i, temperature at which curing is initiated; T_p, temperature at which curing reaches a maximum (peak); T_f, temperature at which curing is completed.

[a] Order of reaction.

[b] Activation energy in kJ mol^{-1}.

Borchardt and Daniels method.[5] The exotherms obtained for various systems ranged between 240° and 330°C. In these systems, the initiation starts at a very high temperature and peak temperature is also quite high. The value of activation energy is in the range of 162–195 kJ mol^{-1}.

The thermal stability of the cured polyurethanes was determined by TGA analysis. Percentage weight loss data reveal that polyurethanes have good thermal stability. IPDT values give the idea of the overall decomposition temperature of the polyurethane systems. Polyurethane with TDI was stable up to 575°C with a char value of 24%. The system with MDI (PU-4) has a char value of 33%. Polyurethanes based on TDI and MDI have more aromatic characteristics and thereby have good flame-retardant properties, which was also supported by their LOI values[6] of 34% and 36%.

The polyurethane films were exposed to UV radiation for 3 h. The λ_{max} values are 367, 360, 363, and 365 nm respectively for PU-1 to PU-4. UV spectra of films were obtained by measuring once every hour. After exposure, no remarkable change in the spectra was observed. Thus it may be inferred that polymers are stable to UV light.[7]

The chemical and hydrolytic stability of the polyurethane systems was measured by dipping the films in methanol, 10% sodium hydroxide, 20% sodium hydroxide, 10% hydrochloric acid, and water. After seven days, only minor changes in weight were observed, while there was no change in the dimension of the films. A slight discoloration of the films was observed in sodium hydroxide solution, but the color of the films remained unchanged in the other media. The weight change data in the range of 0.01–0.04% reveals that the polyurethanes have good chemical and hydrolytic stability.

CONCLUSION

From this study it can be concluded that the polyurethanes possess thermosetting characteristics and they are suitable for flame-retardant applications.

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