Preparation and Properties of Polyimide Foams

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SYNOPSIS

Catalysts for the reaction of aromatic isocyanates with aromatic anhydrides to form imides were investigated using a model reaction. Alkali metal acetylacetone chelate compounds exhibited good catalytic efficiency and selectivity in dimethyl sulfoxide (DMSO). These catalysts were used for the preparation of polyimide foams. The resulting foams exhibited excellent fire resistance and thermal stability. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Aromatic polyimides of various types have been widely used in film and coating applications in increasing amounts because of their superior thermal stability and inherent fire resistance.

Most of these polyimides are prepared by dehydration of polyamic acids formed from aromatic diamines and aromatic dianhydrides.[1-3] An alternative method of polyimide synthesis has been reported in the literature,[4-10] in which polyimides are prepared by the reaction of diisocyanates with dianhydrides. The reaction employed in the literature requires high temperatures, i.e., above 130°C, and a long reaction time to obtain a high molecular weight polymer. In order to reduce the reaction temperature and time, a number of catalysts have been reported in the literature.[11-16]

Similarly, the preparation of polyimide foams has also been studied. Two methods for their preparation have been proposed. The first is by the reaction of a diamine with a dianhydride in an alcoholic solvent.[17-20] The second is by the reaction of a polyisocyanate with a dianhydride, in which the evolving carbon dioxide acts as a blowing agent.[21-24,29-31] The former requires high temperature, i.e., above 200°C, and several process steps to obtain imide foams. The latter also requires high temperature, i.e., above 200°C, in the absence of a catalyst. Even when a catalyst is used, polyols must be added to the po-

lyisocyanate reaction to obtain polyimide foams with uniform cell size at low temperature. The co-use of polyols results in the formation of urethane linkages that decrease the thermal stability of the resulting foams.

In this study, more efficient catalysts were investigated for the reaction of isocyanates with anhydrides. Initially, model compounds were used, followed by polyimide foam preparation without using polyols as reactants.

EXPERIMENTAL

Materials

Phenyl isocyanate (PI) was distilled under reduced pressure prior to use. Phthalic anhydride (PA) was sublimed under reduced pressure. N,N-dimethylformamide (DMF), N,N-dimethylacetamide (DMAc), and N-methyl-2-pyrrolidinone (NMP) were dried over molecular sieves prior to use. Dimethylsulfoxide (DMSO) was distilled over calcium hydride under reduced pressure and stored over molecular sieves. Polymethylene polyphenylene isocyanate (polymeric MDI), 4,4'-diphenylmethane diisocyanate (MDI), and toluene diisocyanate (TDI) were used as received from Dow Chemical Co. Pyromellitic dianhydride (PMDA) and 3,3',4,4'-benzophenone tetracarboxylic dianhydride (BTDA) were used as received form Hüls Inc. and Allco Chemical Corp., respectively. Alkali metal chelate catalysts were synthesized according to the previous paper.[25]

The catalysts employed are listed in Table I.

Table I   Catalysts Employed

Designation	Chemical Identification	Source
Kacac	Potassium acetylacetonate	Synthesized
Na acac	Sodium acetylacetonate	Synthesized
Li acac	Lithium acetylacetonate	Syntehsized
SAK	Potassium salicylaldehyde chelate	Synthesized
SALi	Lithium salicylaldehyde chelate	Synthesized
HAK	Potassium o-hydroxyacetophenone chelate	Synthesized
TPPO	Triphenylphosphine oxide	Aldrich
MPPO	3-Methyl-1-phenyl-2-phospholene-1-oxide	Alfa
Al(O-iPr)₃	Aluminum isopropoxide	Aldrich
AlCl₃-TPPS	Aluminum chloride-triphenylphosphine sulfide	Synthesized
Dabco K-15	Potassium 2-ethylhexanoate	Air Products
Polycat 41	N,N',N''-Tris(dimethylaminopropyl)-sym-hexahydrotriazine	Air Products

Experimental Procedures

Model Systems

In order to follow the reaction rate, the evolved volume of CO_2 was periodically measured with a graduated cylinder connected to the reaction flask and filled with light mineral oil. The cylinder was kept at room temperature during the reaction, and the volume of CO_2 at the standard conditions was calculated from that at room temperature.

The system was flushed with dry nitrogen. Phthalic anhydride (0.01 mol) and catalyst (0.2 mmol) were mixed under a constant flow of nitrogen with 10 mL of solvent in a 100 mL flask equipped with a thermometer, reflux condenser, attached CO_2 measuring unit, dropping funnel, stirrer, and heating mantle. Phenyl isocyanate (0.01 mol) in 2 mL of solvent was added dropwise to the anhydride solution at 50°C over a period of 5 min. The start of the reaction was observed by the evolution of CO_2. The conversion of the reaction was determined periodically from the volume of CO_2 evolved. After cooling to room temperature, the resulting crystals were filtered, washed with a small amount of 1,4-dioxane and a large amount of isopropyl alcohol, and dried under reduced pressure.

The filtrate and the residual liquid after washing with 1,4-dioxane were collected and analyzed by high performance liquid chromatography (HPLC) to determine the concentrations of the various species present in the solution.

HPLC Analysis

Pure compounds of the anticipated reaction products, such as N-phenylphthalimide, N,N'-N'-tri-

phenylisocyanurate, and N,N'-diphenylurea, were synthesized by common methods.

A Perkin Elmer LC-65T HPLC was used for the analysis. NOVA-PAC CN radical-PAC cartridge (8 mm ϕ × 10 cm, Water) was chosen as the column and a UV spectrophotometer was used as the detector (254 nm). A 10 μL sample loop was connected to the Rheodyne high pressure sample injector (Model 7125) to ensure the same volume injection for each sample.

The eluent consisted of a mixture of 1,4-dioxane and n-heptane (15/85 volume ratio) at a flow rate of 1 mL/min.

Polymer Systems

A dianhydride (0.01 mol) and a catalyst (0.4 mmol) were dissolved in 20 mL of DMSO. Into this solution, a diisocyanate (0.01 mol) in 4 mL of DMSO was
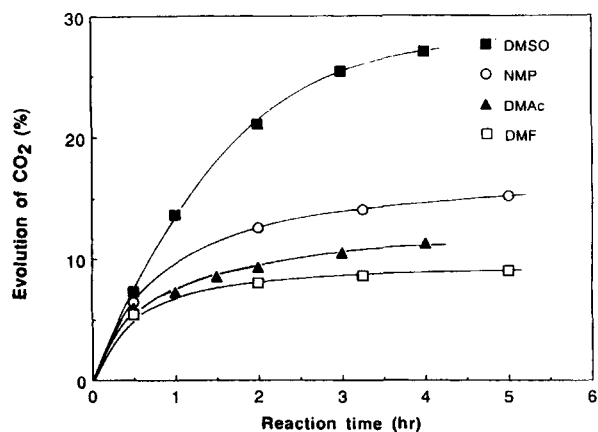
Figure 1   Effect of solvent on the model reaction at 50°C without catalyst.
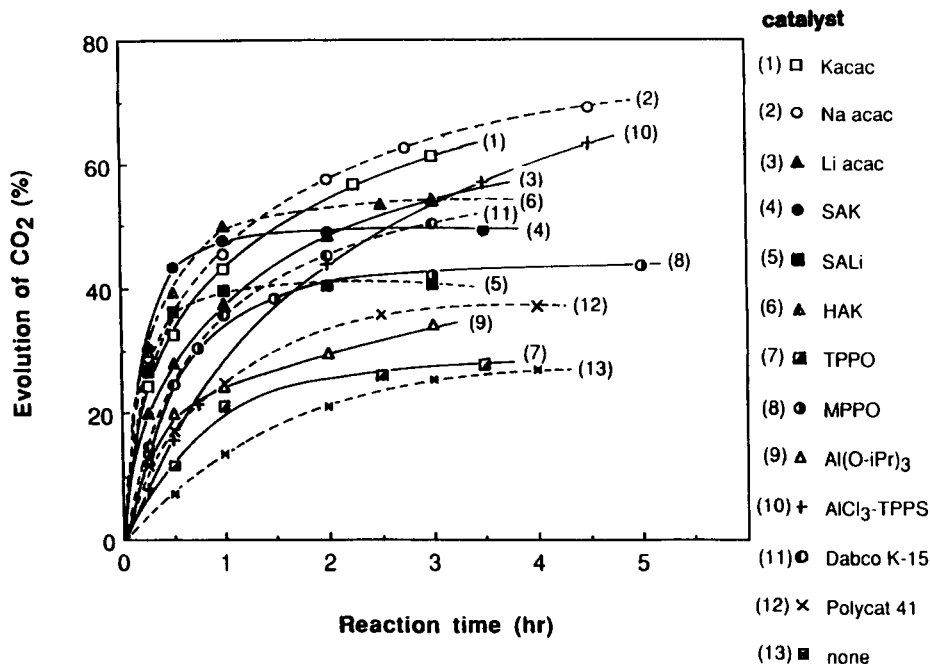
catalyst

(1) □ Kacac

(2) ○ Na acac

(3) ▲ Li acac

(4) ● SAK

(5) ■ SALi

(6) ▲ HAK

(7) ◪ TPPO

(8) ◐ MPPO

(9) △ Al(O-iPr)$_3$

(10) + AlCl$_3$-TPPS

(11) ◑ Dabco K-15

(12) × Polycat 41

(13) ■ none

Figure 2 Effect of catalysts on the model reaction at 50°C in DMSO.

added dropwise at the designated temperature. A vigorous evolution of CO_2 was observed soon after the addition, and more than 90% of the stoichiometric volume of CO_2 was evolved within 20 min. When MDI was employed as the diisocyanate, a yellow precipitate was observed within 10 min. The reaction was carried out until the evolution of CO_2 was no longer detected. The precipitate was collected by filtration, washed with acetone, and dried under reduced pressure at an elevated temperature. When

Table II Effect of Catalyst on Reaction Products of PI with PA at 50°C for 20 h in DMSO

Catalysts	Yield of CO$_2$ (%)	Yield (%)		
		Imide	Isocyanurate	Urea
Kacac	64	61	10	7
Na acac	71	66	12	9
Li acac	62	78	18	6
SAK	49	47	45	0
SALi	42	43	56	0
HAK	56	64	9	7
TPPO	41	55	5	9
MPPO	45	9	0	88
Al(O-iPr)$_3$	61	74	7	2
AlCl$_3$-TPPS	78	58	0	14
Dabco K-15	52	55	39	2
Polycat 41	38	35	57	2

TDI was employed, the reaction mixture was an amber solution. This solution was poured into methanol to form a precipitate, and was analyzed by the procedures described above. Inherent viscosities of the resulting polyimides were measured at a concentration of 0.5 g/dL in conc. H_2SO_4 at 25°C.

Foam Systems

A polymeric MDI was mixed with an equivalent amount of a dianhydride and a surfactant at room temperature by hand mixing. The catalyst dissolved in a solvent was vigorously mixed with the above mixture with a mechanical mixer at the designated temperature, e.g., 70°C. Exothermic foaming occurred soon after mixing. The resulting foam was cured at 70°C for 10 to 20 min. The foam was then heated to remove traces of DMSO.

Foam Properties

The thermal stability of the foams was measured under an air stream on a Thermogravimetric Analyzer (Model 951 DuPont 2100) at a heating rate of 10°C/min.

A Fourier Transform Spectrometer (FTIR Nicolet 5DX) was used for infrared spectroscopy analysis.

The thermal conductivity of the foams was determined on an Anacon Model TCA-8.
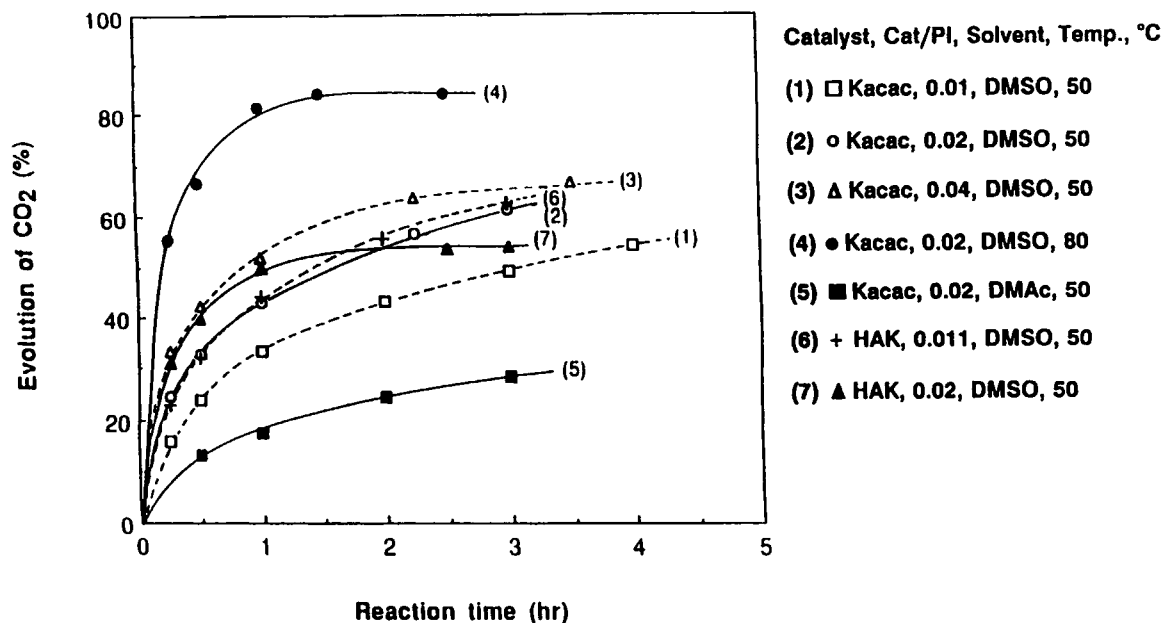
Butler chimney test, oxygen index, friability,

Figure 3   Effect of reaction conditions on the model reaction.

compressive strength, and open cell content of the foams were measured according to ASTM D-3014, D-2863, C-421, D-1621, and D-2856, respectively.

RESULTS AND DISCUSSION

Model Systems

The reaction of phenyl isocyanate with phthalic dianhydride was used as a model reaction, Eq. (1):

$$C_6H_5NCO + \text{(phthalic anhydride)} \rightarrow \text{(N-phenylphthalimide)} \quad N{-}C_6H_5 + CO_2$$

(1)
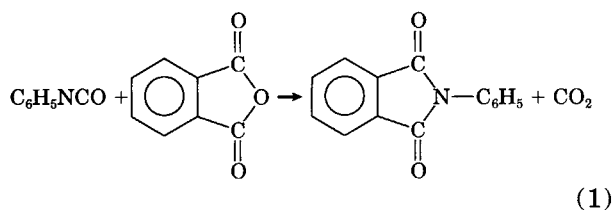
The model reaction was carried out using absolutely dry raw materials; therefore, the CO_2 generated from a trace amount of water in the solvent employed could be ignored.

The reaction rate could be followed readily by measuring the evolution of CO_2. The total yield of N-phenylphthalimide was determined by combining the isolated yield from the reaction mixture and the analytical yield of the reaction solution by HPLC.

The effect of solvent on the reaction rate was investigated at 50°C in the absence of catalyst. The results are shown in Figure 1. It was interesting to note that the model reaction in DMSO exhibited the fastest CO_2 evolution among those in these polar solvents. Reaction of isocyanates with polar solvents, such as DMF[26], DMAc[27], and DMSO[27], are known, but those reactions can occur only at ele-

Table III   Effect of Reaction Condition on Final Reaction Products of PI with PA

Catalyst/PI (mol/mol)	Solvent	Temp. (°C)	Time (h)	CO_2 (%)	Yield (%) Imide	Yield (%) Isocyanurate	Yield (%) Urea
Kacac 0.01	DMSO	50	21	60	65	18	5
Kacac 0.02	DMSO	50	19	64	61	10	7
Kacac 0.04	DMSO	50	20	66	54	10	11
Kacac 0.02	DMSO	80	20	84	81	3	8
Kacac 0.02	DMAc	50	21	63	54	20	11
HAK 0.011	DMSO	50	20	64	65	17	7
HAK 0.02	DMSO	50	20	56	64	9	7

Table IV   Synthesis of Polyimide in the Presence of Catalyst in DMSO at 50°C

Isocyanate	Anhydride	Catalyst	Polymer Solution	Yield (%)	η^{inh} (dL/g)
MDI	PMDA	Kacac	precipitation	92	0.23
MDI	BTDA	Kacac	precipitation	93	0.18
TDI	PMDA	Kacac	clear amber	NA	0.50
TDI	PMDA	SAK	precipitation	NA	NA

vated temperatures, i.e., above 100°C. Consequently, these side reactions can be neglected in this study.

A number of catalysts was investigated in the imide formation reaction. The results are shown in Figure 2 and Table II.

Polycat 41 and Dabco K-15, which are well-known isocyanate trimerization catalysts, accelerated the evolution of CO_2 in the early stage of the reaction. However, large amounts of isocyanurate were detected in the reaction mixture by HPLC analysis. In the presence of isocyanate trimerization catalyst, the formation of the imide linkage would compete with the formation of the isocyanurate

linkage. Similarly, alkali metal chelate catalysts such as Kacac, SAK, and HAK, which were also reported as trimerization catalysts,[25] significantly accelerated the evolution of CO_2. In the case of SAK, the evolution of CO_2 was most vigorous in the early stage of the reaction, but ceased at about 30 min before reaching a high yield of CO_2, and about half the phenyl isocyanate was consumed to form isocyanurate.

On the contrary, in the cases of Kacac and HAK, evolution of CO_2 continued for several hours, and less isocyanurate was formed. The catalytic activity of alkali metal chelates in the selectivity of products
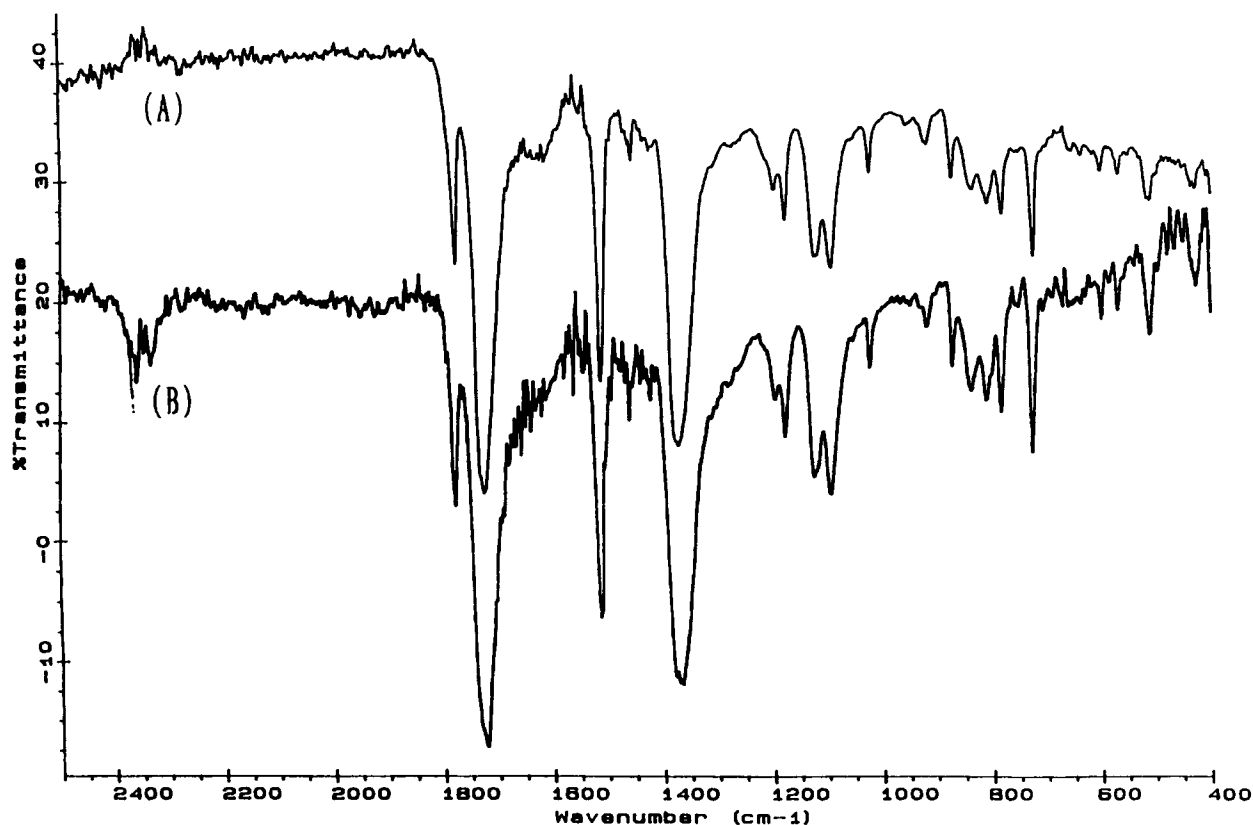
Figure 4   IR spectra of polyimides from MDI and PMDA (A), and polyimide from MDA and PMDA (B).

Table V   Basic Formulation for Imide Foams

Materials	Parts by Weight
PAPI 580*	100
BTDA	116
DC-193**	5
Kacac	varied (2-4)
DMSO	varied (30-100)

Component temperature: 70°C.
* Polymeric MDI, Dow Chem. Co., Functionality: 3.0, %NCO: 30.8.
** Surfactant from Dow Corning Co.

were almost the same, but the percent yield of imide was found to be in the following increasing order: K < Na < Li.

AlCl$_3$-TPPS and Al(O-iPr)$_3$, which are known catalysts for the reaction of phenyl isocyanate with phenylglycidyl ether to form oxazolidone,[28] also accelerated the reaction rate with a small amount of isocyanurate formation. MPPO, which is a known catalyst for carbodiimide formation, did not show any catalytic effects in the imide-forming reaction, but TPPO showed a relatively high yield of imide formation.

Figure 3 and Table III show the effect of the reaction conditions, i.e., catalyst concentration, temperature, and solvent using Kacac and HAK, on the reaction rate and the selectively of products. The reaction rate increased with the concentration of Kacac or HAK. The formation of isocyanurate increased at low concentrations of Kacac or HAK. Both the reaction rate and the selectivity of imide significantly increased at high temperature. The reaction in DMAc resulted in enhanced formation of isocyanurate. These results indicate that the reaction rate and the selectivity of imide are strongly affected by the kind of catalyst, the concentration of catalyst, the reaction temperature, and the solvent employed.

Table VI   Effect of Amount of Kacac on Cell Structure and Thermal Stability of Imide Foams*

Kacac (Part)	Cell Structure	10% Weight Loss Temperature (°C) (as measured by TGA)
2	little coarse	436
3	fine	429
4	very fine	420

* DMSO 70 parts.

Table VII   Effect of Amount of DMSO on Cell Structure and Thermal Stability of Imide Foams*

DMSO (Part)	Cell Structure	10% Weight Loss Temperature (°C) (as measured by TGA)
30	fine	382
50	fine	427
70	coarse	436
100	coarse	456

* Kacac 2 parts.

Polymer Systems

Polyimides were synthesized by the reaction of diisocyanates with dianhydrides based on the results of model systems (Table IV). When MDI was employed as the diisocyanate, only low molecular weight polyimides were obtained. Because the polymers precipitated at an early stage of the reaction, high molecular weight polymers did not result. In the case of TDI, a clear viscous polymer solution was obtained, and relatively high molecular weight

Table VIII   Optimal Formulation for Polyimide Foam and Its Properties

| Ingredients	
PAPI 580	100 parts
BTDA	116
DC-193	5
Kacac	3
DMSO	50
Foaming Profile	
Foaming temperature (°C)	70
Gel time (s)	45
Rise time (s)	130
Tack free time (s)	90
Cure conditions	70°C, 10 min + 130°C, 3 days
Properties	
Density (kg/m^3)	15.5
Open cell content (%)	95
10% Weight loss temperature (°C)	415
Oxygen index (%)	46.5
Butler Chimney test (% wt. retained)	97
Friability (% wt. loss)	15
K-factor (W/m · K)	0.0444
Compressive strength (MPa)	
(∥)	0.057
(⊥)	0.021

polyimide was obtained in the presence of Kacac as catalyst because the asymmetric TDI structure, or steric hindrance of the o-methyl group, of the TDI hindered crystalline products. When SAK was used as the catalyst, a precipitate was observed during the reaction even in the case of TDI. This precipitation would be caused by the formation of isocyanurate as previously mentioned. The infrared spectra of the polyimide prepared from MDI and PMDA in the presence of Kacac and the polyimide prepared from methylene dianiline (MDA) and PMDA are shown in Figure 4. Both spectra show exactly the same absorption, including absorptions at 1780, 1720, and 720 cm^{-1}, which are due to the imide group.

Foam Systems

Unmodified rigid polyimide foams were prepared by a low-temperature process based on the results of the model systems. An aromatic polyisocyanate and an aromatic dianhydride in equivalent amounts were employed with a surfactant, a catalyst, and an organic solvent. Polymeric MDI (PAPI® 580) and

BTDA were used as the polyisocyanate and the dianhydride, respectively. Kacac and DMSO were chosen as the catalyst and solvent, respectively, to achieve the fastest reaction rate at low temperature. A basic formulation is presented in Table V. Foam ingredients were preheated at 70°C before foaming. In order to get uniform cell structure and high thermal stability, the amounts of Kacac and DMSO were optimized. The effects of the amount of Kacac on the cell structure and the thermal stability are shown in Table VI. It is interesting to note that increasing the amount of Kacac resulted in very fine and uniform cells and a negligibly small decrease in thermal stability as measured by TGA. This decrease in thermal stability seems to be caused by decomposition of polyimide accelerated by Kacac catalyst.

The effect of the amount of DMSO on the cell structure and the thermal stability in terms of 10% weight loss temperature as measured by TGA are shown in Table VII. About 30–50 parts of DMSO resulted in fine cell foams. However, increasing amounts of DMSO resulted in less uniform cells and increased thermal stability. From the infrared spectrum, the intensity of the absorptions of unreacted
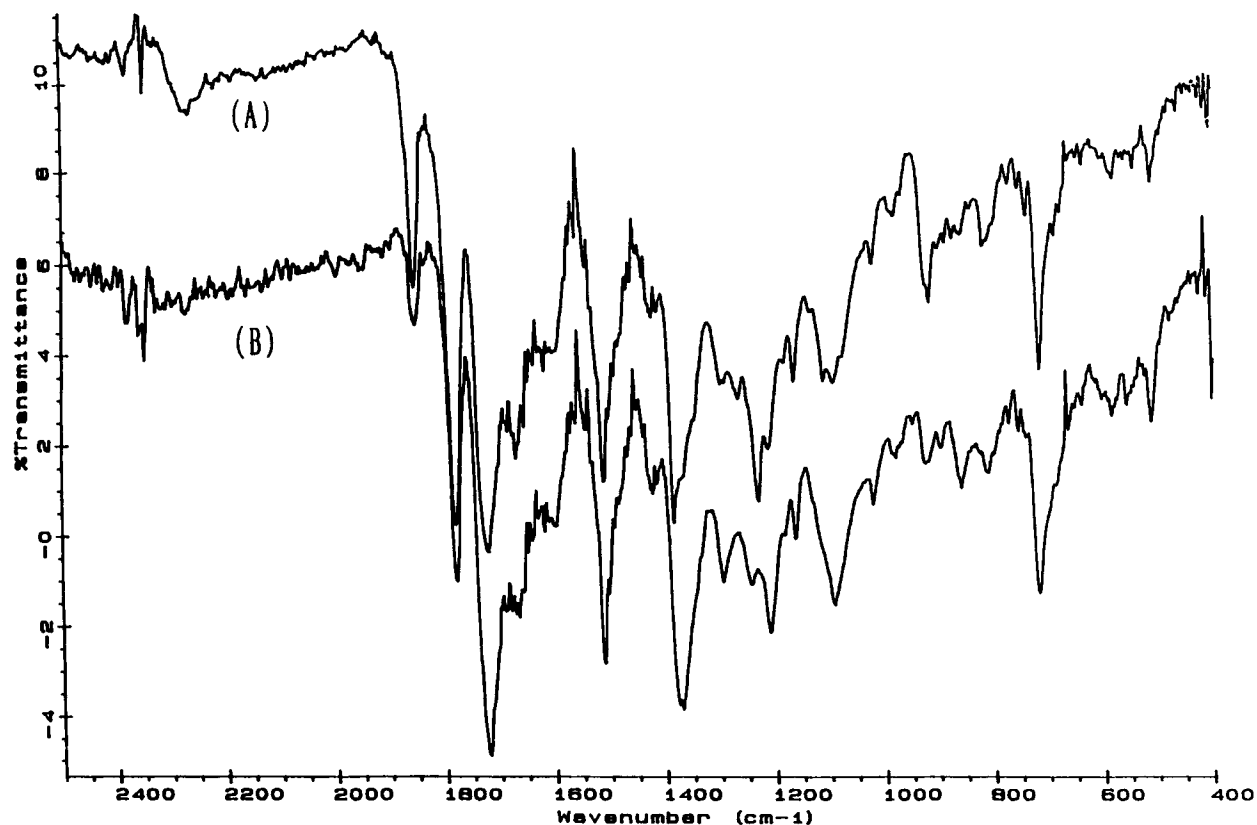
Figure 5   IR spectra of imide foams using Kacac. (A) DMSO 30 parts. (B) DMSO 70 parts.
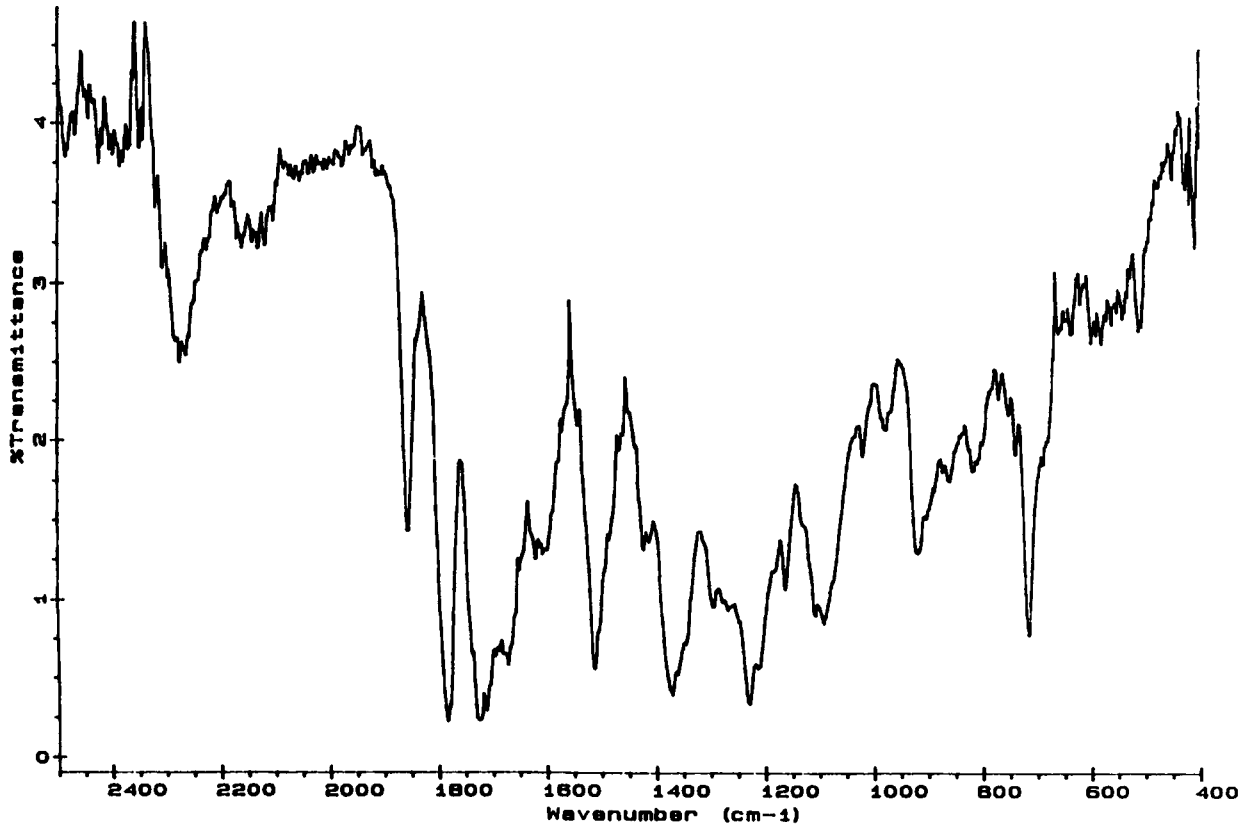
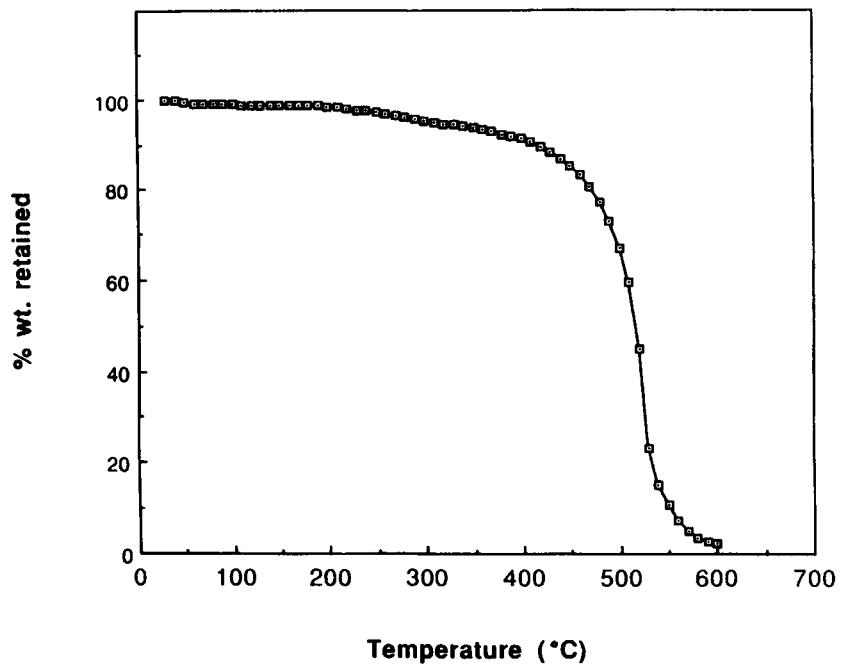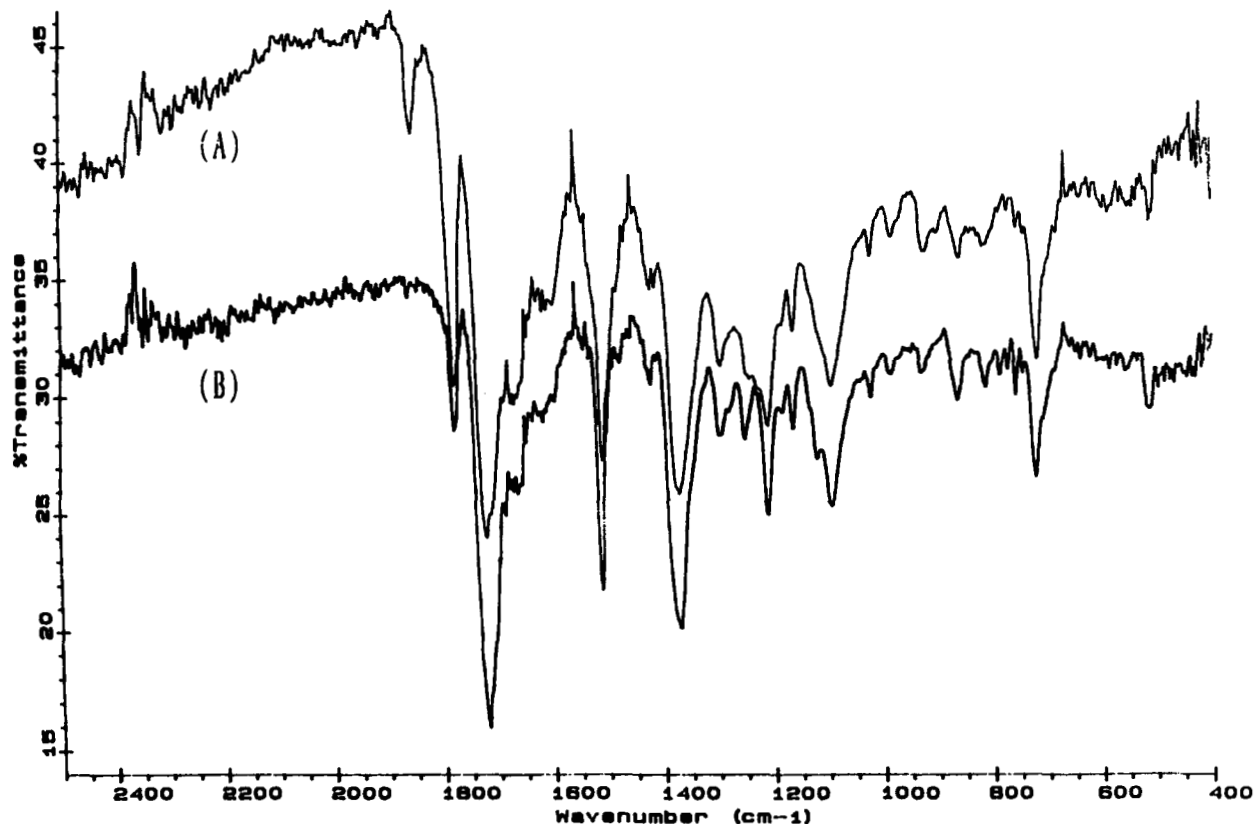**Figure 6**   IR spectrum of imide foam using SAK.

Figure 7   TGA of polyimide foam.

Figure 8   IR spectra of imide foams from polymeric MDI and BTDA (A), and polyimide from MDI and BTDA (B).

(2270 cm^{-1}) NCO and anhydride groups (1850 cm^{-1}) tended to decrease with increasing amount of DMSO (Fig. 5). With sufficient DMSO, the reaction of isocyanates with anhydrides could be completed, resulting in high thermal stability. When SAK was employed as the catalyst instead of Kacac, a uniform cell structure was also obtained, but its infrared spectrum contained the absorptions of isocyanurate group at 1710, 1415, and 755 cm^{-1}, as could be expected from the results of the model systems. Absorption of carbodiimide at 2140 cm^{-1} was also observed (Fig. 6). An optimal formulation for polyimide foam was attained and is shown in Table VIII with the foaming profile and the foam properties. Needless to say, no blowing agents were added because polyimide linkage formation and CO_2 gas generation occur simultaneously. TGA data showed that the 10% weight loss temperature was 415°C (Fig. 7), and the oxygen index was 46.5. These properties indicated the superior thermal stability and fire resistance of the foam. The infrared spectrum of this foam is shown in Figure 8, compared with polyimide polymer prepared from MDI or polymeric MDI and

BTDA. Both spectra were very similar, except for the absorption of the unreacted anhydride group at 1850 cm^{-1}, and showed absorptions of imide group, but no isocyanurate group. When PMDA was employed as the dianhydride, the resulting foam collapsed or contained large voids because of too much CO_2 evolution.

CONCLUSIONS

Alkali metal chelate compounds exhibited efficient catalytic activities for the reaction of isocyanates with anhydrides to form imide linkages. The reaction rate and the selectivity of imide formation were strongly affected by the catalyst concentration, the reaction temperature, and the solvent employed. An unmodified polyimide foam was attained from polymeric MDI and BTDA in the presence of Kacac and DMSO without the addition of a blowing agent, and exhibited excellent fire resistance and thermal stability, i.e., the 10% weight loss temperature as mea-

sured by TGA was 415°C and the oxygen index was 46.5.

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