

Synthesis of Poly(*p*-diphenylmethylerphthalamide) from Recycled Monomers

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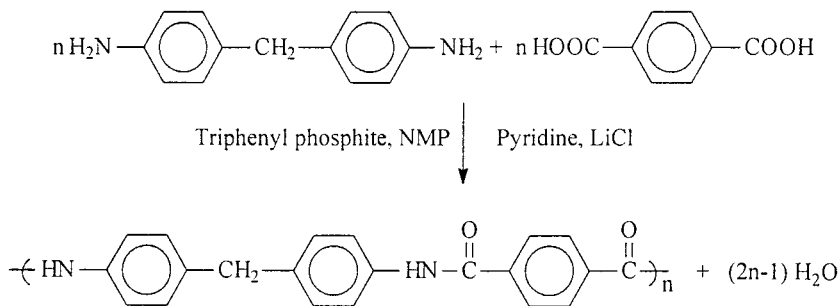
ABSTRACT: Poly(*p*-diphenylmethylerphthalamide) or PMA was synthesized from the reaction between recycled terephthalic acid (TPA) and recycled 4,4'-methylenedianiline (MDA) in the presence of pyridine, triphenyl phosphite, and a solubilizing-aid agent. The reaction conditions used for this polymerization were determined from a model reaction using pure TPA and pure MDA as reactants. It was found that PMA with the highest % yield and molecular weight was obtained when the mixture of lithium chloride (LiCl) and calcium chloride (CaCl₂) were used as solubilizing-aid agents with a reaction time of 4 h. Recycled TPA with 92% purity was obtained from acid hydrolysis of waste

PET bottles using sulfuric acid as a catalyst at 150°C for 5 h. Recycled MDA with 99% purity was obtained from aminolysis of rigid polyurethane foam scrap using diethylenetriamine as a degrading agent at 180°C for 70 min. PMAs prepared from recycled monomers exhibited thermal properties, which were comparable to those of PMA prepared from pure monomers. However, due to a possibility of several isomers present in recycled MDA, PMAs prepared from this monomer had lower melting points and thermal decomposition temperatures than those prepared from pure MDA. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 3723–3729, 2003

INTRODUCTION

Poly(*p*-diphenylmethylerphthalamide) or PMA is an aromatic polyamide generally used to improve several properties of some polymers. For example, it is used to improve thermal and mechanical properties of Nylon 6 by copolymerization. It is also used to prepare copolymers with Kevlar® to improve that polymer's processibility. PMA is obtained from the reaction between terephthalic acid (TPA) and 4,4'-methylenedianiline

(MDA) in the presence of a catalyst such as triphenylphosphite and a solubilizing-aid agent such as lithium chloride (LiCl), as shown below.^{1–3} There is also an application using a combination of LiCl and CaCl₂ as a solubilizing-aid agent for PMA synthesis because this combination was found to be effective for synthesizing poly(*p*-phenyleneterephthalamide); however, no comparison between the effectiveness of these solubilizing-aid agents for PMA synthesis was done.^{4,5}



The objective of this research is to find a suitable reaction time and a type of solubilizing-aid agent for

PMA preparation, and to study the potential of using recycled monomers instead of pure monomers to prepare such polymer. Because pure TPA and MDA are synthesized from products obtained from petrochemical resources, these resources continuously declined due to high consumption. Consequently, an attempt to use other resources has been developed. One resource is plastic waste. Chemical recycling of plastic waste gives the products that can be used as reactants for

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preparations of other chemicals and polymers. For example, poly(ethylene terephthalate) or PET are depolymerized by reactions such as glycolysis⁶⁻⁸ and hydrolysis.^{9,10} The obtained products from these reactions are predominantly the monomers of PET such as TPA, ethylene glycol (EG), or bis(hydroxyethyl) terephthalate (BHET).⁶⁻¹⁰ On the other hand, aminolysis of certain polyurethanes (PU) can yield MDA.^{11,12} Therefore, in this research, PMAs were prepared from both pure and recycled TPAs and MDAs, and their thermal properties were studied.

EXPERIMENTAL

Materials

In acid hydrolysis process, waste PET bottles (both water and soft-drink bottles), conc. sulfuric acid solution, ammonia solution, and conc. hydrochloric acid (HCl) were used. These chemicals except waste PET bottles were obtained from Fluka. TPA (analytical grade) from Fluka and TPA (commercial grade) from Siam Mitsui PTA Co., Ltd. were used as references for characterization.

For aminolysis, rigid polyurethane foam scrap donated from the DOW Company, diethylenetriamine (DETA) and cyclohexane purchased from Fluka were used. Practical grade MDA from Fluka was used as references for characterization.

In synthesis of PMA, *N,N'*-methylpyrrolidone (NMP) (AR grade), triphenylphosphite, anhydrous calcium chloride (CaCl_2) (AR grade), LiCl (AR grade), pyridine (AR grade), and methanol from Fluka were used. The reference PMA was prepared using pure TPA and pure MDA.

Methods

Depolymerization of PET

Ground PET bottles 1.6 g and 24 mL of 10 M aq. H_2SO_4 solution were mixed in a 500-mL four-necked round-bottom flask equipped with a stirrer, a thermometer, a condenser, and an N_2 gas inlet. The reaction was carried out at 150°C under nitrogen atmosphere for 5 h. The solution was then diluted with distilled water. The precipitate was filtered, washed with distilled water, and dried at 100°C for 6 h. The dried precipitate was dissolved in 500 mL of 5 M aq. NH_3 solution. The unreacted PET was precipitated out of the solution. It was filtered and dried at 100°C for 6 h, while 80 mL of conc. HCl solution was added to the filtrate and TPA was then precipitated. TPA was collected, washed, with distilled water two to three times and dried at 110°C for 6 h.

Characterization of recycled TPA

Functional group analysis of the product was carried out using FTIR spectroscopy (FTIR Spectrometer

Model Nicolet-Impact 400) and the obtained IR-spectrum was compared with those of analytical and commercial TPA.

% Purity of TPA was characterized using HPLC (Lichrocart-C 18 column with size of 250×4 mL, mobile phase = 80/20 acetonitrile/water).

Depolymerization of PU

DETA 50 g was put in a 500-mL four-necked round-bottom flask equipped with a stirrer, a thermometer, a condenser, and an N_2 gas inlet. It was heated and maintained at the temperature of 180°C. Ground PU 100 g was then added into the flask. The reaction time was maintained for 70 min. MDA was then extracted from the solution using cyclohexane and distilled water. The cyclohexane layer was left at room temperature for 7 days for crystallization. MDA was collected and put in a desiccator.

Characterization of recycled MDA

% Purity of MDA were determined using HPLC (Lichrospher-100 RP18 column with size of 125×4 mL, mobile phase = 35/65 acetonitrile/water with ammonium acetate).

Functional group analysis was carried out using FTIR spectroscopy (FTIR Spectrometer Model Nicolet-Impact 400) and the obtained IR-spectrum was compared with that of practical grade MDA.

Synthesis and characterization of PMA from pure monomers

CaCl_2 3.75 g and LiCl 1.25 g were dissolved in a mixture of NMP 125 mL and pyridine 25 mL. Then the obtained mixture, pure TPA 4.15 g and pure MDA 4.95 g and triphenylphosphite 18 mL were mixed at 110°C for 2-4 h. The product was poured in excess methanol, and PMA was precipitated. PMA was filtered, washed with warm water and methanol, and dried at 120°C for 24 h. The process was repeated but using only CaCl_2 5 g and LiCl 5 g, respectively. Then the amounts of all products were determined by weighing and their functional groups were analyzed by FTIR spectroscopy (FTIR Spectrometer Model Nicolet-Impact 400). The viscosities of PMA solution were determined by Brookfield viscometer using NMP with 5% LiCl as solvent.

Synthesis and characterization of PMA from recycled monomers

Recycled TPA and MDA were used to prepare PMA using the suitable conditions as described above. Then

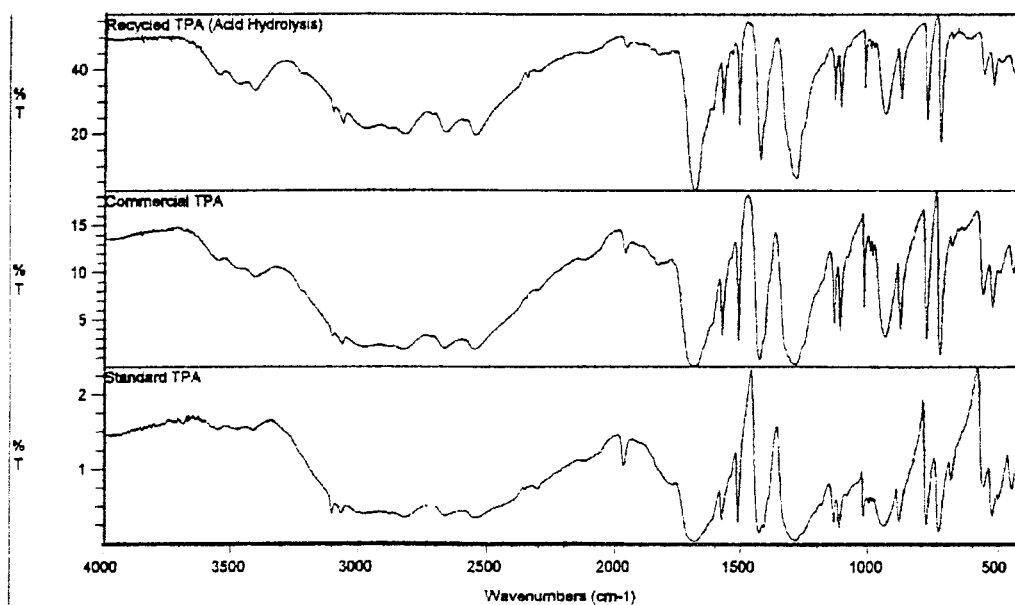


Figure 1 FTIR spectra of synthesized, commercial, and analytical TPAs.

functional groups of the obtained PMA were characterized using FTIR spectroscopy (FTIR Spectrometer Model Nicolet-Impact 400), and its thermal properties were characterized using DSC and TGA techniques (Perkin-Elmer DSC 7 and TGA 7) using heating rates of 20°C/min. The viscosities of PMA solution were determined by a Brookfield viscometer using NMP with 5% LiCl as solvent.

RESULTS AND DISCUSSION

Depolymerization of PET and characterization of TPA

The FTIR spectra in Figure 1 show that the product obtained from acid hydrolysis of waste PET bottles has the same characteristic peaks as commercial and analytical TPAs. These characteristic peaks corre-

spond to aromatic rings are at wave numbers of 700–800 cm^{-1} and 1680 cm^{-1} , while the characteristic peaks correspond to carboxylic groups are at wave numbers of 1300, 1440, and 2500–3,100 cm^{-1} (broad). This suggests that the obtained product is TPA because its spectra are similar to those of commercial and analytical TPAs. The purity determined from HPLC was 92%. Impurity contaminated by the TPA may possibly be oxalic acid, an oxidized product of EG by oxygen.¹³ EG was another product obtained besides TPA from acid hydrolysis of PET.¹⁰

Depolymerization of PU and characterization of MDA

From FTIR spectra shown in Figure 2, it can be seen that the white solid obtained from chemical recycling

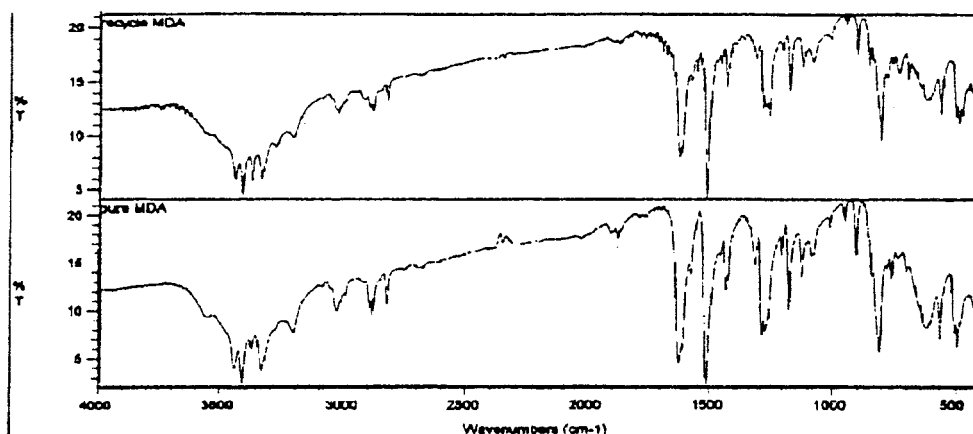


Figure 2 FTIR spectra of synthesized and practical grade MDAs.

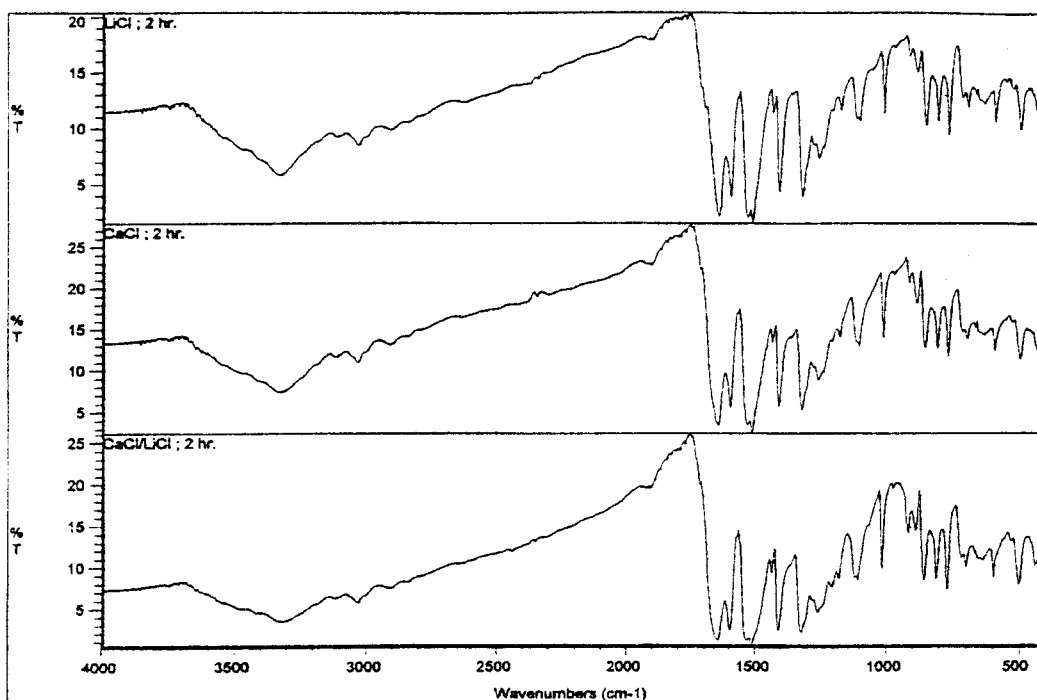


Figure 3 FTIR spectra of PMAs prepared in the presence of LiCl, CaCl₂, and a mixture of CaCl₂ and LiCl using a reaction time of 2 h.

of PU has the same characteristic peaks of MDA as those obtained from practical grade MDA. These characteristic peaks of NH₂ groups are at wave

numbers of 3200–3500 cm⁻¹ (broad), and those of aromatic rings are at wave numbers of 800 and 1620 cm⁻¹. Purity determined from HPLC was 99%.

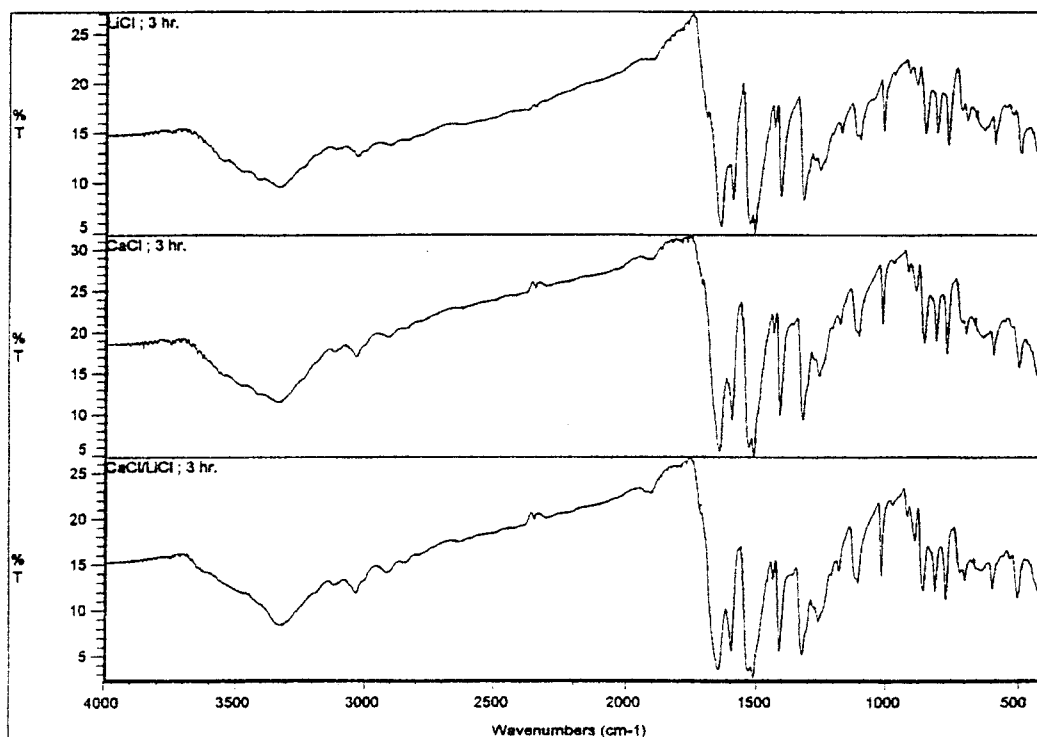


Figure 4 FTIR spectra of PMAs prepared in the presence of LiCl, CaCl₂, and a mixture of CaCl₂ and LiCl using a reaction time of 3 h.

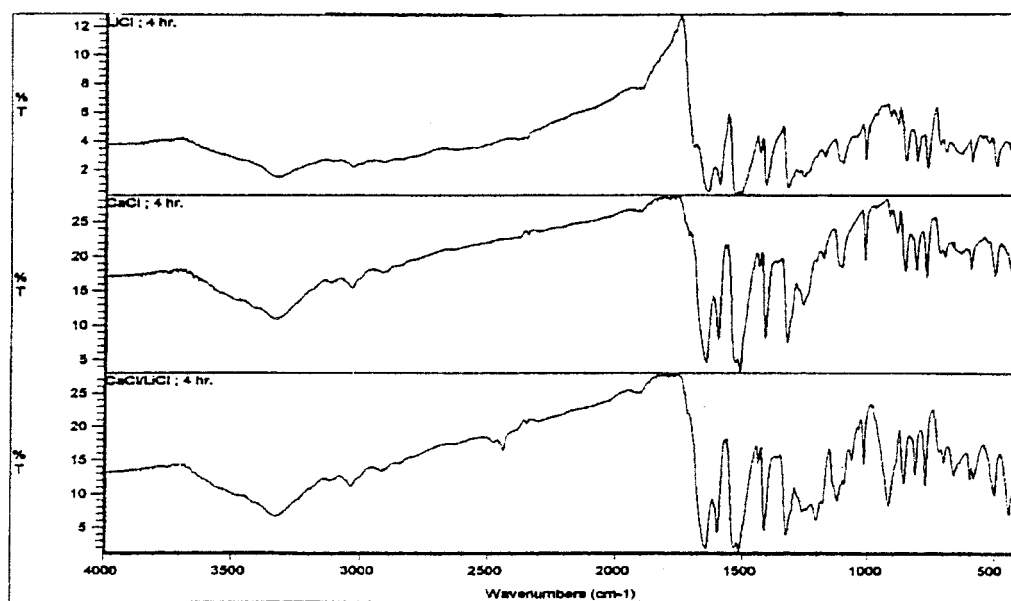


Figure 5 FTIR spectra of PMAs prepared in the presence of LiCl, CaCl₂, and a mixture of CaCl₂ and LiCl using a reaction time of 4 h.

Synthesis and characterization of PMA from pure monomers

The FTIR spectra of PMA synthesized with different reaction times of 2, 3, and 4 h are shown in Figures 3–5, respectively. It can be seen that all the spectra show characteristic peaks of PMA at wave numbers of 1650 and 1540 cm⁻¹, which correspond to the carbonyl group of amide linkage and at a wave number of 3300 cm⁻¹, which corresponds to the primary amine of the amide linkage. This indicates that the reaction time and the type of solubilizing-aid agent did not affect the chemical structure of the obtained PMAs.

However, it is clearly seen from Table I that in the case of using CaCl₂ and a mixture of CaCl₂ and LiCl as the solubilizing-aid agents, the longer the reaction time was used, the higher the yield and the molecular weight (increase in viscosities) obtained. On the other hand, when LiCl was used, the yield was highest at the

reaction time of 3 h and decreased at the reaction time of 4 h, indicating the possible reversible reaction. Because the polymers started degrading during the drying process, they were not used for viscosity determination.

The results also indicate that CaCl₂ seems to be better solubilizing-aid agent than LiCl. This may be because CaCl₂ has a higher ability to increase solubility of PMA than LiCl; as a result, the polymerizable polymer chains of the former case were maintained in the solution for a longer time. Furthermore, as previously reported for poly(*p*-phenyleneterephthalamide) synthesis by Higashi and coworkers, CaCl₂ can form a complex, CaCl₂ · nPy (Py = pyridine), which also favors polymerization reaction.⁴ When a mixture of CaCl₂ and LiCl was used, the amounts of the obtained PMAs were comparable to those of PMAs prepared from CaCl₂ but the molecular weights of the former case were slightly higher. This indicated that a double salt complex, CaCl₂ · LiCl · nPy,⁴ formed in the system was more effective in promoting the reaction than CaCl₂ · nPy. However, CaCl₂ · LiCl · nPy showed a significant effect only when the reaction time is 4 h. These conditions also give highest amount of PMA; therefore, they were used for synthesis of PMA from recycled monomers (Table II).

TABLE I

Amount of PMA Prepared from Pure Monomers

Metal chloride	Reaction time (h)	% Yield (%)	Average viscosity (cps)
CaCl ₂	2	93	1.9
	3	94	2.1
	4	96	2.2
LiCl	2	82	^a
	3	83	^a
	4	67	^a
CaCl ₂ + LiCl	2	92	2.2
	3	93	2.3
	4	99	Not dissolved

^a No experiment was done.

Synthesis and characterization of PMA from recycled monomers

It can be seen that the amounts of PMA prepared from both recycled monomers are slightly lower than those prepared from pure monomers and the combination of the pure and recycled monomers. DSC results show no PMAs glass transitions, and their melting points are above 500°C. This suggests that PMA is highly

TABLE II
Amounts and Thermal Properties of PMA Prepared
from Pure and Recycled Monomers

Types of monomers	% Yield (%)	T_g (°C)	T_m (°C)	Average viscosity (cps)
Pure TPA + Pure MDA	99	—	534	Not dissolved
Recycled TPA + Pure MDA	99	—	535	Not dissolved
Pure TPA + Recycled MDA	99	—	517	Not dissolved
Recycled TPA + Recycled MDA	98	—	510	Not dissolved

crystalline polymer. TGA thermograms in Figure 6 indicate that all PMAs have thermal decomposition temperatures below 500°C. This means that PMAs degrade before melting. This phenomenon is due to the chemical structure of PMA, which is highly regular and tightly bound by hydrogen bonds. However, thermal behaviors of PMAs prepared from recycled MDA with pure TPA and recycled TPA were different from those prepared from pure MDA with pure TPA and recycled TPA. It can be seen that the former PMAs exhibit lower melting and decomposition temperatures than the latter ones. In addition, FTIR spectra, shown in Figure 7, indicate that the chemical structures of PMAs prepared from recycled MDA with pure TPA and recycled TPA were different from those prepared from pure MDA with pure TPA and recycled TPA.

It can be seen that these differences are caused by recycled MDA. This suggests a possibility of the presence

of other substances than the expected 4,4'-MDA in recycled MDA. However, according to 99% purity of recycled MDA from HPLC analysis and the similarity in FTIR spectra of recycled and practical grade MDAs shown in Figure 2, these contaminated substances must have same molecular weights and same functional groups as 4,4'-MDA. When considering the polymerization process of PU used in this experiment, this PU is synthesized from the reaction between ethylene glycol and diphenylmethane diisocyanate (MDI). MDI preparation process from formaldehyde, aniline, and phosgene yields several isomers, as shown below.^{14,15} Consequently, when the mixture of isomeric MDIs is used in polymerization of PU, the chemical recycling of PU would result in the mixture of isomeric MDAs. When this recycled mixture was used to prepare PMA, the chemical structures of the obtained PMAs were altered,

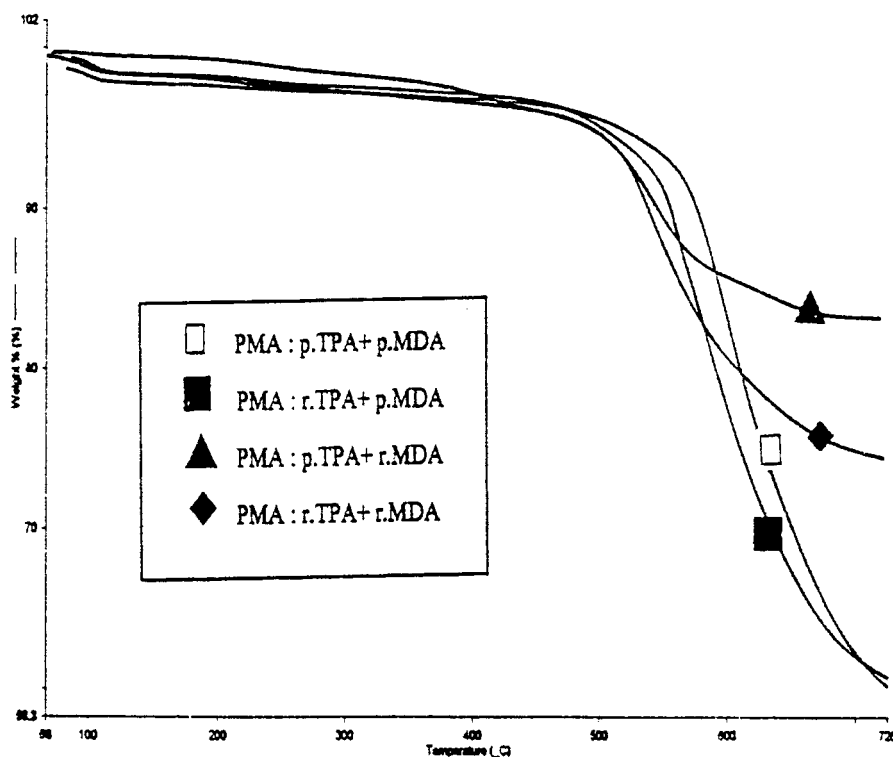


Figure 6 TGA thermograms of PMAs prepared from the recycled and pure monomers.

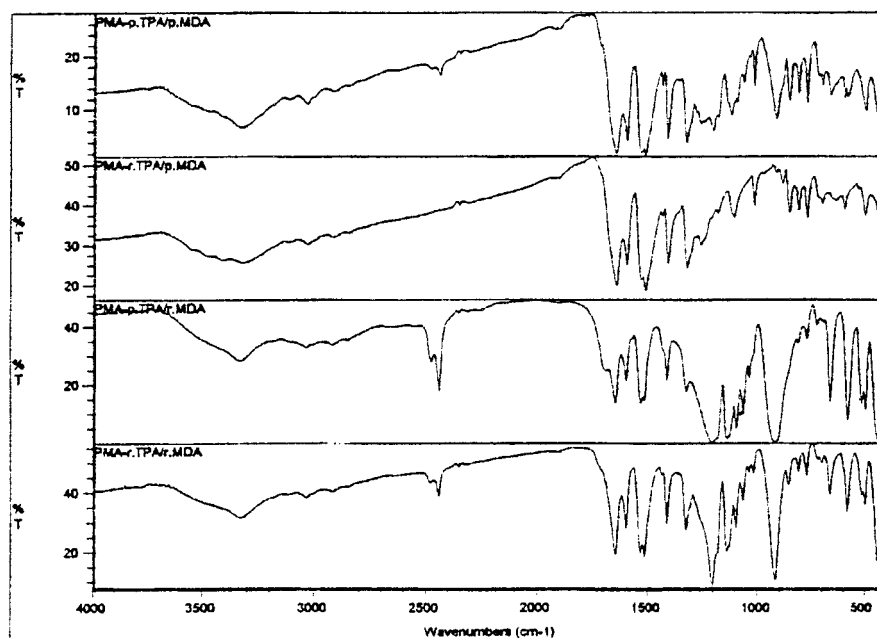
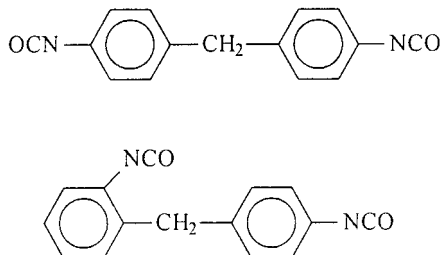


Figure 7 FTIR spectra of PMAs prepared from recycled and pure monomers.

and this structural irregularity can lower their melting and decomposition temperatures.



The above results suggest that TPA and MDA obtained from chemical recycling of waste PET bottles and rigid PU foam scrap, respectively, can be used to prepare PMA having the properties that are comparable to PMA prepared from pure TPA and MDA. Therefore, this method can be used as an alternative way to prepare PMA.

CONCLUSION

PMA with 99% yield can be synthesized from the reaction between recycled TPA and recycled MDA in the presence of pyridine, triphenyl phosphite, and the mixture of LiCl and CaCl₂ using a reaction time of 4 h. It was found that PMA prepared from recycled TPA and pure MDA exhibited thermal stability that were comparable to those of PMA prepared from pure monomers. On the other hand, PMAs prepared from

recycled MDA with recycled TPA and pure TPA had lower melting points and thermal decomposition temperatures than PMA prepared from pure monomers.

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