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Properties and Structures of Terephthalyl Chloride (TPC) Modified meta-Aramid Copolymers

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The properties and structures of terephthalyl chloride (TPC) modified poly (m-phenylene isophthalamide) (PMIA) with TPC mole content in acylchloride from 5%–15% were studied in this paper. The composition and structure of the copolymer were determined by ^{1}H NMR. The content of TPC moiety in the molecular chain was calculated. Thermogravimetric analysis (TGA) and Fourier transform infrared (FTIR) were used to analysis the thermal properties of TPC modified PMIA copolymer. The results show that by introducing TPC units in the PMIA molecular chain, PMIA copolymers with better thermal properties were prepared. With the increase of TPC content, the TPC modified PMIA exhibit increasing thermal stability. The pyrolysis process of the copolymer was detected by FTIR spectra. When the copolymers were pyrolyzed to 500°C, an aryl nitrile band at 2230 cm^{-1} appears in the FTIR spectrum. This means that at this temperature breakage of the amide bond occurred.

Keywords terephthalyl chloride (TIC), meta-aramid copolymers

Introduction

Poly(m-phenyleneisophthalamide) (PMIA) is an important material with excellent thermal and oxidative stability, flame resistance, and dielectric behavior. PMIA is prepared from the low-temperature polycondensation of m-phenylenediamine (MPD) and isophthaloyl chloride (IPC) in an amide solvent. It is the base polymer for Nomex aramid fiber products commercialized by E.I. Dupont de Nemours and Co. and Teijinconex fiber by Teijin Ltd. Since its commercialization in 1967, it has been used in a wide variety of applications, including protective apparel, filtrations and thermal-resistant furnishings (1). Many efforts were made to improve the properties of PMIA by physical and chemical methods. For this reason, modification by copolymerization with a third monomer is usually applied (2). The introduction of a new monomer changes the molecular structure of the meta-aramid polymer to improve its properties. Xylylene diamine was used to copolymerize with MPD and IPC to improve the dyeing property

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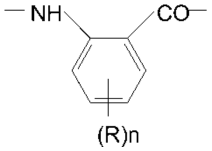
without losing excellent heat-resisting property (3). In a Teijin Ltd patent, the segment



was introduced in the molecular chain of PMIA (4). This can improve the dye properties of the polymer and at the same time the good heat-resistant properties still remained. In China, Chai Mingzhong reported that the copolymer of MPD, IPC and 2,5-dichloro-l,4-benzenedicarbonyl chloride (DDC) exhibited better flame resistant properties than PMIA (5).

In this paper, we prepared a series of meta-aramid copolymers of terephthalyl chloride (TPC) with MPD and IPC. The TPC content of the diamine was at most 15 mole% of the entire diamine. Low temperature solution polycondensation in DMAc was used. The composition of the copolymer was determined by ^{1}H-NMR. The effect of TPC content on the inherent viscosity is discussed. Finally, the thermal properties of TPC modified PMIA copolymer were investigated.

Experimental

Raw Materials and Chemical Reagents

IPC, MPD, and TPC were commercially available and were distilled before use. The melting points of the monomers used in this reaction were 142–143, 62.5–63 and 43–44°C, respectively. DMAc from Shanghai No. 1 Chemical Reagent Factory was dewatered by a molecular sieve so that the water content was not above 0.05%.

Synthesis Procedure

The experimental procedure included: (1) dissolving MPD in DMAc, (2) cooling the solution to -10°C, (3) adding TPC and part of IPC slowly to the system under stirring, (4) 10 min later, adding the rest of the IPC to the system and immediately removing the ice bath (5). After the reaction was finished, $Ca(OH)_2$ was added to neutralize the HCl from the reaction.

Viscosity Determination of Copolymer

The inherent viscosity η_{inh} was measured at a concentration of $c = 0.5$ g/dL in 98% sulfuric acid at 30°C and calculated with Formula (1):

$$\eta_{inh} = \frac{\ln t_1/t_0}{c} \tag{1}$$

where t, t_0 are flow time of the dilute solution and solvent, respectively.

Fourier Transform Infrared (FTIR) Spectrum

FTIR absorption spectra were obtained in a Nicolet NEXUS-670 spectrometer. 13 mm diameter pellets of KBr with a sample weight of 120 mg were used. The spectra shown are the result of a scan range from 4000-400 cm^{-1} at a resolution of 9 cm^{-1}.

^{1}H-NMR

A Bruker AV 400 spectrometer was used to get NMR spectra at scan times of 16 and solvent of DMSO.

Thermogravimetric Analysis (TG)

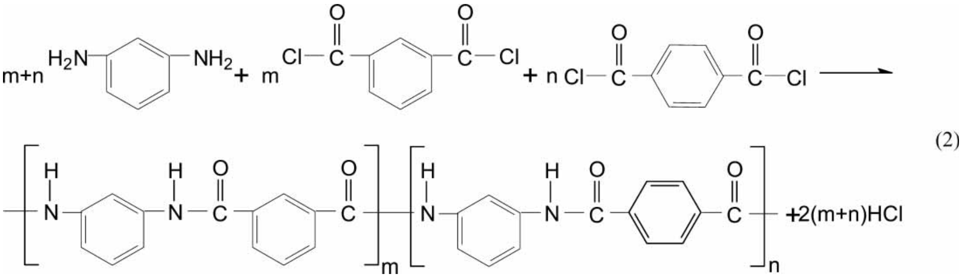
A Perkin-Elmer-7 was used for thermogravimetry (TG) measurements. A constant flow of 20 cm^3/min of Nitrogen (99.999%) was used. Heating rates of 20°/min were applied over the temperature interval of 25–800°C.

Pyrolysis

Samples that were pyrolyzed to different selected temperature were prepared in the same muffle furnace with an approximate heating rate of 15°C. Rapid cooling to room temperature under a nitrogen atmosphere effectively stopped the pyrolysis process.

Results and Discussion

We prepared a series of meta-copolyamides containing TPC moiety of the composition as shown in Formula (2):



(2)

where m and n are mole fractions, $n < 15\%$ and $m + n = 100\%$.

The Effect of TPC Content on the η_{inh} of the Copolyamides

The relationship of η_{inh} of TPC modified PMIA with TPC content is shown in Figure 1. The other reaction conditions were reaction concentration of 1 mol/L(MPD), initial reaction temperature of −10°C and maximum reaction time of 80 min. First, with the increase of the TPC content, the η_{inh} of the copolyamides decreases slightly from 1.68 to 1.56 for TPC from 5% to 15%. The reason may be that the introduction of a third monomer of TPC destroyed the good order of the chain conformation, however this effect was very small, and possibly because the third monomer content in the molecular chain is not high enough to produce an effect on the whole molecular structure. As for the PMIA, in the whole molecular chain, the amide linkages are attached to two

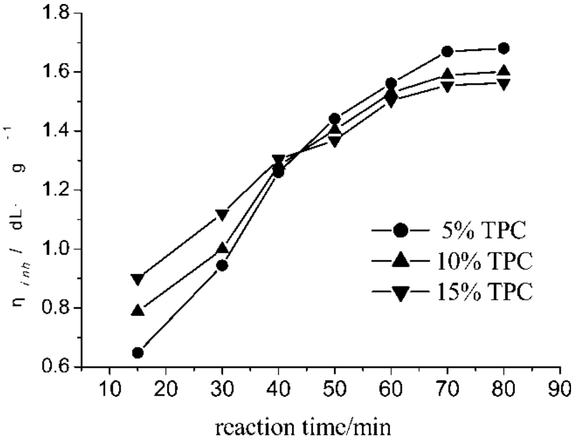
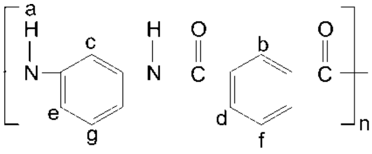


Figure 1. The relationship between inherent viscosity of TPC modified PMIA and TPC content.

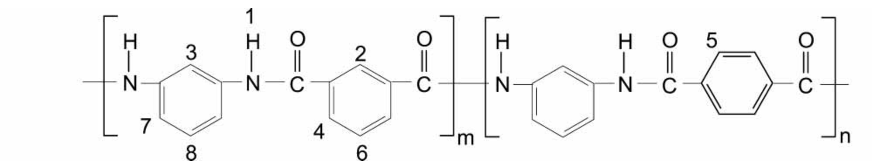
aromatic rings at the meta position. However, for the TPC modified PMIA, the amide linkages are partly randomly attached to aromatic rings at the para-position. Thirdly, in the early stage of reaction, the η_{inh} of copolymers increased with increasing TPC content, which was opposite to the effect for the final products. We think this is due to the relative reactivity of TPC and IPC. According to the synthesis procedure, 50% of the IPC was first reacted with MPD to form polymer with end groups of NH_2. Then, TPC and the remaining IPC was added in the reaction system. Both the TPC and IPC can react with end group NH_2. With an increase in TPC content, the η_{inh} of the copolymer increases. This means the reactivity of TPC with MPD is greater than that of IPC, but because the polycondensation is an equivalent reaction, the difference between the η_{inh} of final TPC modified PMIA became rather small after the equilibrium was reached.

^{1}H-NMR Analysis of Copolymer Structure

^{1}H-NMR spectrum of PMIA resin and copolyamide with TPC content n = 10% are shown in Figure 2. The chemical shifts and peak areas are shown in Tables 1 and 2. The chemical structure of PMIA and TPC modified PMIA were shown in Formulae (3) and (4).



(3)



(4)

The peaks a-g of PMIA in Figure 2 correspond to the protons a-g marked in Formula (3) (6). Comparing the spectra of PMIA and TPC modified PMIA, it can be seen that most

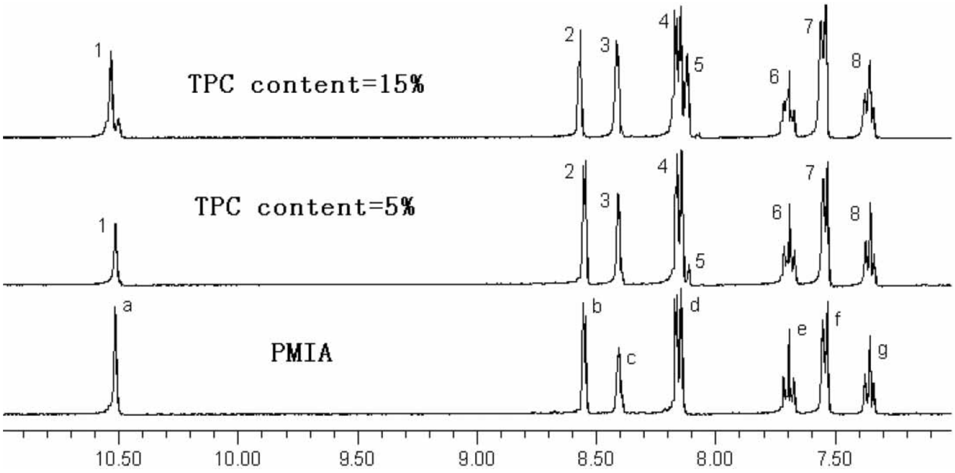


Figure 2. ^{1}H-NMR spectrum of PMIA and TPC modified PMIA copolymer.

parts of them are similar. In the spectrum of modified PMIA a small peak, 5, appeared just besides peak 4, which results from proton 5. With the increase of TPC content, the area of it increased. When the TPC content was 5%, the single line of peak 1 was assumed to result from protons 1. The single lines of peak 2 and 3 belong to the protons 2 or 3. The intensity ratio of peak 3 to 2 was 100:84.7, which was similar to the mole ratio of MPD:IPC:TPC (100:85:15). According to this, we know peaks 2 and 3 belong to protons 2 and 3, respectively. Guided by the spin-spin coupling rule, protons 4 and 7 were a 2 multiplet. By calculating the peak areas, the intensity ratio of 4 to 7 is 85.3:100, which was similar to the ratio of proton 4 to 7. So we know peaks 4 and 7 correspond to proton 4 and 7. For the same reason, protons 6 and 8 were a 3 multiplet; this corresponds to peak 6 and 8. At last, the area of peak 5 was 1, which corresponds to the mole ratio of TPC.

From the NMR spectra, it is clear that the reaction of the third monomer TPC with MPD and IPC occurred and the TPC modified PMIA copolymer was obtained. With different mole ratios, the relative intensity of the different protons changes in proportion.

TG Analysis of TPC Modified PMIA

Figure 3 shows the TGA curves obtained during pyrolysis of TPC modified PMIA under nitrogen with a heating rate 20°C/min. The TGA curve of pure PMIA is also shown.

Table 1

Chemical shift and peak area of ^{1}H-NMR spectrum of PMIA

Peak no.	Chemical shift (ppm)	Peak area	Peak no.	Chemical shift (ppm)	Peak area
1	10.52	1	5	7.69	1.14
2	8.55	1.14	6	7.53	2.1
3	8.41	1.12	7	7.36	1.26
4	8.17	2.13			

Table 2

Chemical shift and peak area of ^{1}H-NMR spectrum of TPC modified PMIA with n = 15%

Peak no.	Chemical shift (ppm)	Peak area	Peak no.	Chemical shift (ppm)	Peak area
1	10.55	1.33	5	8.12	1.00
2	8.55	1.33	6	7.69	1.33
3	8.41	1.57	7	7.55	3.14
4	8.15	2.68	8	7.36	1.54

Some key features of the TPC modified PMIA TGA curves are shown in Table 3. The first mass loss occurred from room temperature to 100°C, due to the release of adsorbed moisture. No further changes were observed until about 314°C depending on the TPC content. The major mass loss begins at about 340°C. The TPC modified PMIA with TPC content of 5% and 10% have higher onset temperature than that of PMIA. Two steps are observed in the TGA curve of PMIA when temperature increases from 350°C to 600°C. Whereas for TPC modified PMIA, these two stages are not evident. At 600°C, PMIA decomposed almost completely. But the weight retained of TPC modified PMIA with TPC content of 10% and 15% was 10% and 42%, respectively, at this temperature. So the introduction of TPC as a third monomer can improve the thermal stability of PMIA.

Infrared Spectroscopy Measurement of the Pyrolysis of PDDA Modified PMIA

The FTIR spectrum of TPC modified PMIA with TPC content of 15% is shown in Figure 4. The main absorption bands are listed in Table 4. The spectra of samples heated to different temperatures arranged from 350°C to 750°C are also shown in Figure 4.

The FTIR spectrum of the sample heated to 350°C is very similar to that of untreated samples. The number and position of the absorption bands almost did not change except for a slight shift to higher wavenumber of the N-H stretching absorption band. The reason is the breaking of hydrogen bonds linked to the amide bond. There is no obvious change in

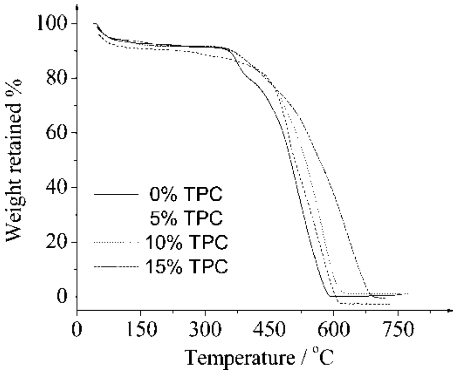


Figure 3. TG curves of PMIA and TPC modified PMIA.

Table 3
Some key features of PDDA modified PMIA TG curves

Sample	Decomposition temperature/°C	Temperature of 15% wt retained/°C	Temperature of 50% wt retained/°C	Weight retained at 550°C/%
TPC content 5%	314	353	562	52
TPC content 10%	363	396	738	65
TPC content 15%	372	433	780	69
Nomex fiber	355	377	499	17

the FTIR spectrum of pyrolysis sample until the temperature reaches 470°C. When the TPC modified PMIA was heated to 500°C, an aryl nitrile band at 2230 cm^{-1} appears in the FTIR spectrum and most of the rest of the peaks disappear. This means that at this time the amide bond was broken. When the pyrolysis temperature reaches 600°C, the 1447 cm^{-1} amide bond disappeared completely. Of the characteristic absorption bands of the benzene ring, just one remained, at 1608 cm^{-1}, and this band became broader with the increase of pyrolysis temperature. When the temperature reached 700°C, the aryl nitrile band disappeared because of the decomposition of the matter formed in the pyrolysis process.

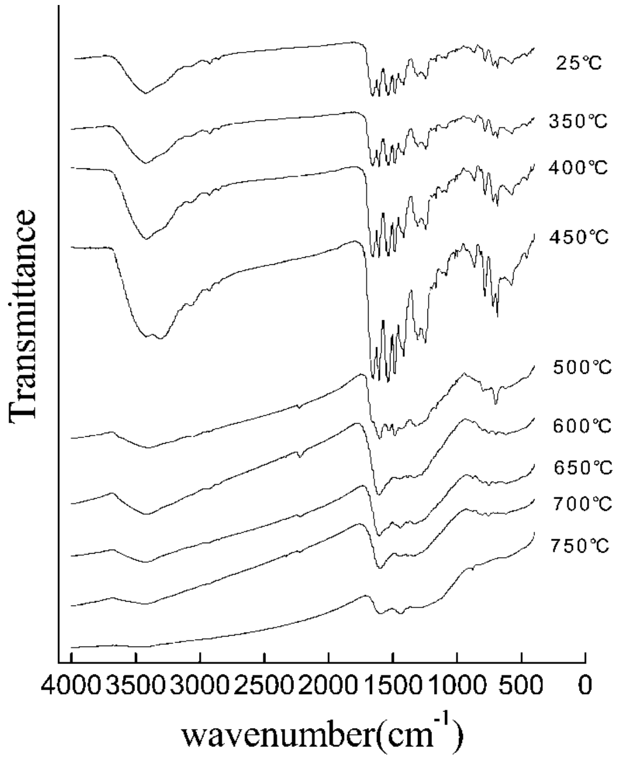


Figure 4. The FTIR spectrum of TPC modified PMIA pyrolysis samples.

Table 4
The IR bands of TPC modified PMIA

Wavenumber/cm^{-1}	Vibrations
3307	N-H stretching
3077	C-H stretching
1667	Amide C=O stretching
1610	C=C stretching
1545	N-H deformation and C-N stretching
1325	Aromatic C-N stretching
1248	Coupling of C-N stretching and N-H bending
784 and 687	Out-of-plane C-H
721	N-H deformation

Conclusions

TPC modified poly(m-phenylene isophthalamide) with TPC mole content from 5% to 15% were prepared by the method of low-temperature-solution condensation polymerization. With the increase of the third monomer TPC content, the inherent viscosity of TPC modified PMIA copolymer decrease slightly. ^{1}H NMR was used to characterize the TPC modified PMIA copolymer. The chemical shift of different protons on the molecular chain was defined. The content of TPC moiety in the molecular chain can be calculated. The result of TGA curves and pyrolysis process showed that by introducing TPC moiety in the PMIA molecular chain, PMIA copolymers with better thermal properties were prepared. With the increase of TPC content, the TPC modified PMIA exhibit increasing thermal stability. The pyrolysis process was characterized by FTIR spectrum. When the copolymer was pyrolized to 500°C, an aryl nitrile band at 2230 cm^{-1} appears in the FTIR spectrum. This means that at this temperature amide bonds were broken.

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