STM JOURNALS

Research & Reviews: Journal of Physics
ISSN: 2278–2265 (Online), ISSN: 2347-9973 (Print)
Volume 7, Issue 3
www.stmjournals.com

Spectroscopic, Thermal and Morphological Properties of Pa6 Copolymers

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Abstract

Spectroscopic, thermal and morphological properties of PA6/PA12 copolymers have been reported in the present study. FTIR studies indicate the chemical interaction occurring between PA6 and PA12 homopolymers. Thermal properties of copolymers have been investigated by DTA technique. Among the PA6 copolymer, hydrolyzed PA6 has more Tg and Tm then the copolymer. Thermal degradation of copolymer is studied by TGA and DTG technique. The studies suggest that hydrolyzed PA6 has more thermal stability of the copolymer. X-ray diffractograms of PA6 copolymer have been recorded. The studies suggested that hydrolysed PA6 has more crystalline structure and has high degree of crystallinity with the increase of PA12 content. The degree of crystallinity is found to decrease with decrease of PA6 content.

Keywords: *Gamma ray studies, degradation studies, Polyamide 6 (PA6), Polyamide 12 (PA12), Morphology and Thermal studies.*

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INTRODUCTION

Ruxandra *et al.* have studied irradiation effects on PA6 properties using chemiluminescence and dielectric spectroscopy, and dielectric properties were measured for PA6 irradiated to 100 kGy radiation dose [1].

Zaharescu *et al*. have irradiated PA6 with electron beam and investigated thermal degradation using FTIR technique and proposed that durability is more in air than in water [2].

Radiation effects on polyamides have been reviewed by Porubska [3]. Polyamides are irradiated with gamma rays electron beam: change in chemical structure, mechanical properties thermal resistance, water absorption has been reported.

Radiation cross linking of bio-based polyamide has been investigated by Zhang *et al*. in the dose range of 50–20 kGy [4]. Variation in crystalline has been investigated by IR and XRD techniques. Relation between solution fraction and radiation dose is found to follow Charles by Pinner equation.

Influence of electron beam irradiation on electrical properties of PA6 and PA12 has been reported by Zhao *et al*. [5]. An increase in Ac breakdown strength is observed and cross linking of polymers has resulted in reduction of dielectric constant.

Mizera *et al*. have investigated radiation induced cross-linking properties of industrial polymer like polypropylene (PP), polyamide6 (PA6), PA6,6 etc. [6]. Significant changes in mechanical and thermal properties are observed. The tensile strength and elastic modulus are observed to increase with radiation. Thermal stability is also reported to improve after irradiation.

Aranburu and Eguiazabal showed that blends of PA6/PP have gained importance as after combination of thermomechanical properties

of polyamides with processability of PP compatible agents are added to improve compatibility [7, 8]. No change in glass transition temperature (Tg) of PA12 phase is observed. No change in Tm is observed. Addition of compatibilization led to decreases of particle size and increase in ductility. Young's modulus shows synergistic behavior for all the compositions.

Luo *et al.* [9] have reported gamma irradiation effects in PA6/PTFE blends in the radiation dose range of 0–100 kGy [9]. Gamma irradiation is reported to improve tensile modulus, tensile strength and flexural modulus is found to increase while moisture absorption decreases with increase of PTFE content and irradiation dose.

Effects of gamma irradiation on optical properties of different commercial packing film were reported by Moura and Ortiz in the dose range of 0–100 kGy [10]. UV/VIS spectra are recorded before and after irradiation. A red shift in the wavelength of spectrum is observed with the increase of radiation dose.

Gamma irradiation effect in binary blends of polyethylene of different types with PA6 was reported by Albano *et al*. using electron spin resonance, diffraction scanning colorimitry, Fourier transform infrared techniques to elucidate structural modification on irradiation [11]. The studies suggest the formation of allyl, alkyl and polyenyl radicals' presence of carboxyl group after irradiation of polymer is observed.

Radiation effects in lower density poly ethylene/ethylene vinyl acetate blends have been reported by Siqin *et al*. using DSC, TGA and solubility measurement [12]. Radiation aging behavior of PA6/EPDM blends has been reported by Zahrescu *et al*. using isothermal and non-isothermal chemiluminescence and FTIR techniques [13]. The chemiluminescences peak is observed at 120°C corresponding to higher oxidation rates under non-isothermal conditions, presence of free radicals was also confirmed by CL studies.

EXPERIMENTAL TECHNIQUES

Designation of Samples

PA6, PA12 copolymers with different compositions are investigated in the present studies. They are designated in the Table 1.

RESULTS AND DISCUSSION

DTA Analysis

Thermal properties PA6/PA12 copolymers are evaluated using differential thermal analysis as shown in Figure 1. Curves 1, 2, 3 and 4 represent the DTA curves of differential thermal analysis. DTA is applied to PA6/PA12 copolymer to evaluate thermal properties. Curves 1, 2, 3, 4, 5 and 6 in Figure 1 represent DTA curves of PA1, PA2, PA3.1 and PA3 respectively. Thermal properties like T_g and T_m are as listed in the following Table 2.

Table 1: *Different Compositions of PA6 and PA12 Copolymer.*

S. No.	Composition of PA6	Composition of PA12	Designation of Copolymer
1	100 hydrolyses	-	PA1
2	100 6 non-hydrolyses	-	PA2
3	95 70 20	5 30 80	PA3 PA3.1 PA4
4	30	70	PA5
5	5	95	PA6

Table 2: *Thermal Properties of PA6 and PA12 Copolymer.*

S. No.	Sample	Glass Transition Temperature (Tg)	Melting Temperature (T_m)
1	PA1	45	220
2	PA2	50	216
3	PA3.1	55	210
4	PA3	38	207

T_g of PA6 lies in the range of 45–50° while its melting point is around 220°C.

Correspondingly, the T_g of copolymer lies in the range of 40–55°C, depending on the composition of PA12, while T_m of copolymer drastically reduces to 160 from 220°C with the increase of PA12 content incorporation of PA12 into polymer. Results in distraction of hydroxyl bond causing a reduction in Tg and Tm.

Thermal Degradation Profile of Copolymers

The thermal degradation behavior of PA6 copolymer has been investigated using thermo gravimetric (TGA) technique. The TGA thermogram of PA6 and its copolymers are as shown in Figure 2: The curves of PA1, PA2, PA3.1 and PA3 respectively.

The copolymers are observed to degrade thermally in three different stages as shown in Figure 2. Temperatures at which 5, 50 and 100% decompositions (T_5, T_{50} and T_{100}%) occur, are listed in Table 3.

The data suggest that the copolymer with more PA6 content has more T5, T50 and T100% values than the remaining copolymer. Due to copolymerization, interplanar hydrogen bonding might have destroyed causing crystalline destruction. Therefore it is appropriated to expect less thermal stability for the copolymer with more PA12 content. The result suggest that due to the presence of hydroxyl bands, the values of T_5, T_{50} and T_{100} are higher for PA1; with the incorporation of PA12, the hydrogen bonds are destroyed causing a reduction in decomposition temperature copolymers.

Table 3: *Thermal Decomposition Temperature of PA6/PA12 Copolymers.*

S. No.	Sample	Thermal Decomposition Stages		
		T_5%	T_{50}%	T_{100}%
1	PA1	300	420	490
2	PA2	300	400	480
3	PA3	300	350	400
4	PA3.1	290	300	450

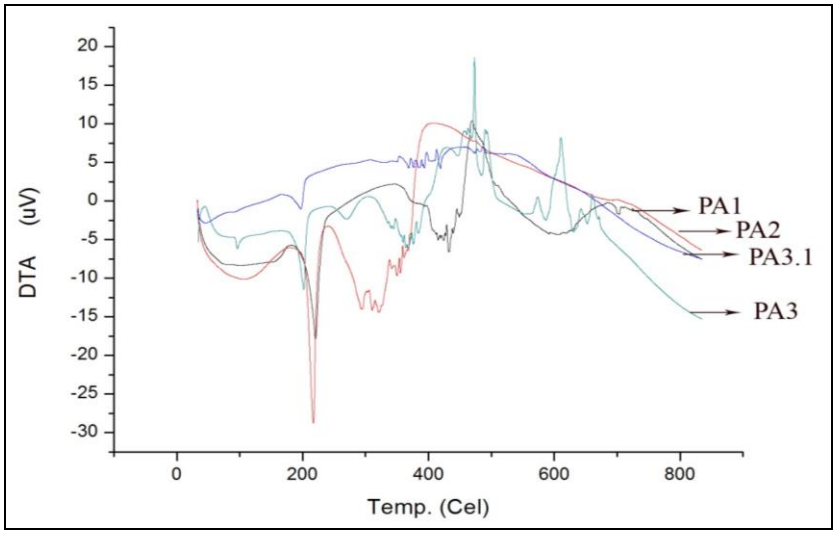

Fig. 1: *DTA Curves.*

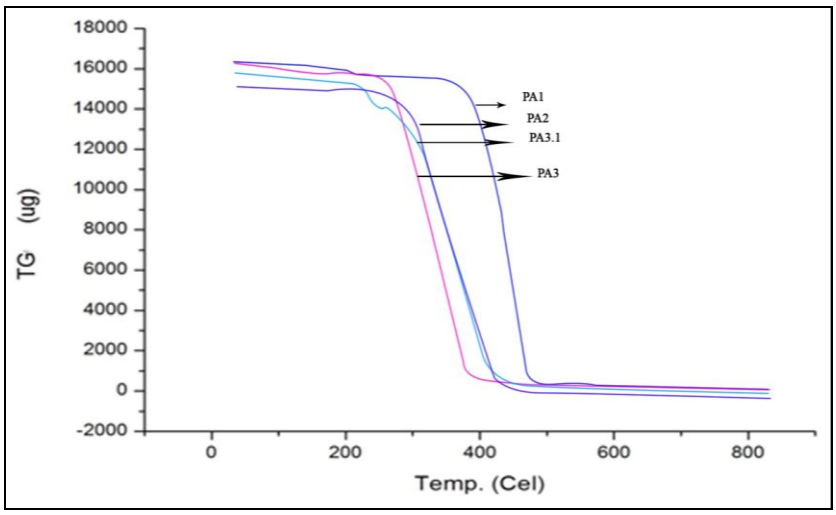

Fig. 2: *TGA Thermogram of PA6/PA12 Copolymers.*

DTG Analysis

DTG thermograms of PA6 copolymers are shown in Figure 3. Different stages of thermal degradation are as given in Table 4. Correspondingly, DTG curves of PA1 have a high T_{100}% at 120°C, while $T_{100\%}$ is at 380°C for nonhydrolysed PA6. The broadness of DTG peaks for PA1 and PA2 are large; while the peak width becomes very narrow for the copolymers which suggests that the copolymers have less thermal stability.

XRD Studies

X-ray diffractograms of PA6 and its copolymers are shown as Curves 1, 2, 3, 4 and 5 in Figure 4. Peak position and d-spacing are as given in the Table 5.

PA6 is reported to exist in two crystalline form called as α_1 and α_2, which gives well distinct diffraction peaks centered around (2θ) values of 19.5 and 21.0°, corresponding to (200), (002) planes of α1 and α2 phase; while there exist γ-phase which gives diffraction peak centered on 23°C corresponding (020) plane [14,15].

In the present study, PA6 copolymer exhibits the three different peaks of α_1, α_2 and γ-phases. The copolymers with more PA6 content have shown α_1 and α_2 peaks centered around 2θ values 19–19.5°, and 2θ values 23.5–23.4°. The copolymer with less PA6 content or more PA12 content exhibits the γ-phase centered around 2θ value of 21°.

The values of d-spacing are increased with the increase of PA12 content or decrease of PA6 content. The result suggests that increase in crystal size dimension results in an increase of randomness of macromolecular chains. The results are further confirmed by measuring degree of crystallinity X_c as shown in Table 5, which is low for the copolymer with low PA6 content or high PA12 content.

Table 4: *Different Stages of Thermal Degradation.*

S. No.	Sample	Stages (°C)		
		I	II	III
1	PA1	220	340	420
2	PA2	219	315	380
3	PA3.1	-	275	425
4	PA6	-	275	-

Table 5: *XRD Data of PA6 Copolymers*

S. No.	Sample	Peak Position 2θθ	FWHM	d-spacing (nm)	X_c
1	PA1	19.61 23.55	0.3149 0.3936	4.525 3.776	-
2	PA2	19.61 23.55	0.3149 0.3936	4.525 3.776	-
3	PA3	19.61 23.55	0.3149 0.3936	4.525 3.776	0.209
4	PA3.1	19.6836 23.4871	0.3146 0.3986	4.519 3.791	0.197
5	PA4	21.096	0.5760	4.2078	0.236
6	PA6	21.055	0.576	4.215	0.447

FWHM= Full Width at Half Maximum, X_c =Degree of Crystallinity.

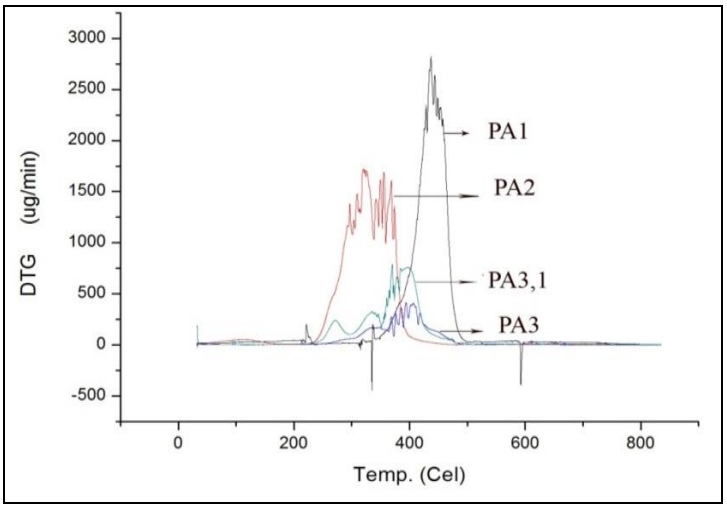

Fig. 3: *Differential Thermo Gravimetric Analysis (DTG) of PA6 Copolymers.*

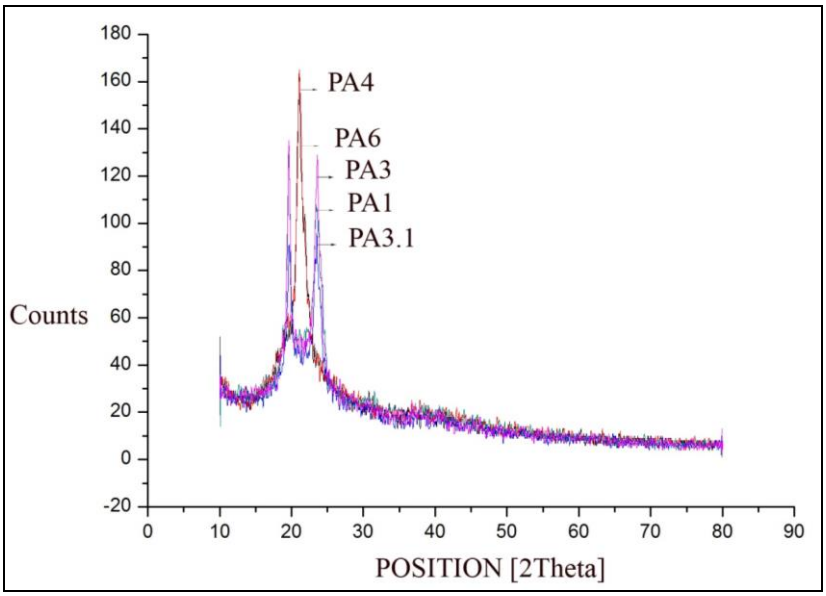

Fig. 4: *X-Ray Diffractograms of PA6 Copolymers.*

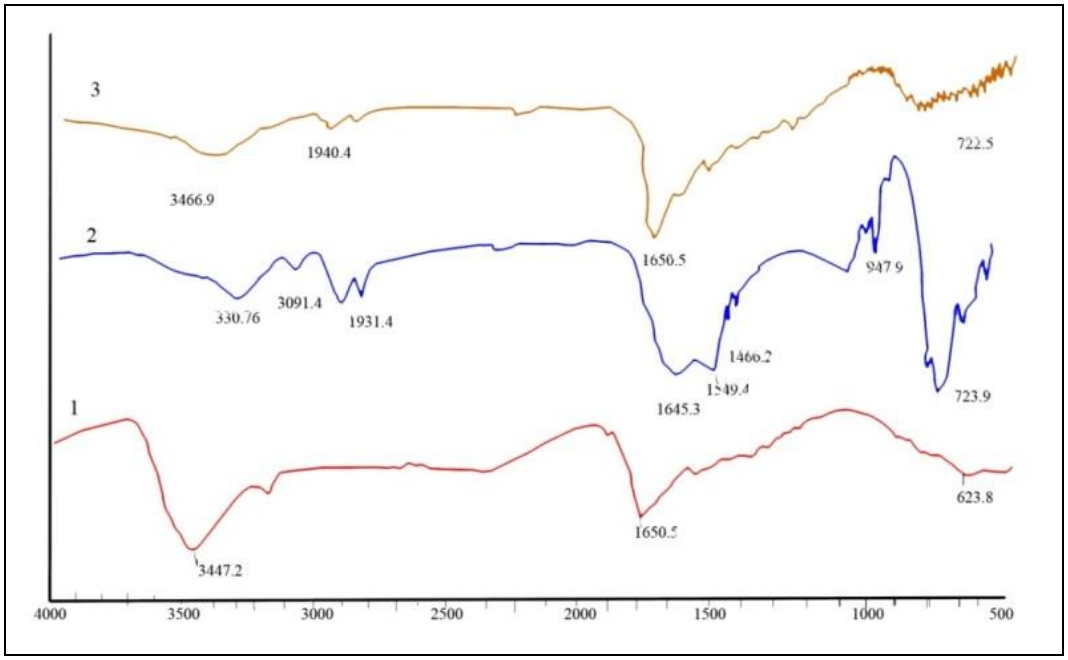

Fig. 5: *FTIR Spectra of PA6/PA12 Copolymer with Different Compositions: Curve 1 5/95, Curve 2 10/90, and Curve 3 20/80.*

FTIR Studies

FTIR spectra of PA6 and its copolymers are recorded to identify chemical changes induced by copolymerization. The Figures 5 and 6 represent the FTIR spectra of PA6 homo-polymer and PA6/PA12 copolymers of 5/95, 10/90, 20/80, 50/50, 70/30, 80/20, 90/10 and 95/5 compositions; while Figure 7 corresponds to the FTIR spectra of PA12 homo-polymer. The spectra possess various absorption bonds corresponding to the chemical structure of both homo-polymers. More prominent bands among them are 3400, 3300, 3150, 2940, 2850, 1650, 1540, 1460, 1370, 1280 and 720 cm^{-1} position. These absorption bands are categorized into following groups: (i) $CONH_2$ groups, (ii) N-H symmetric and asymmetric vibration, (iii) CH_2/CH_3 groups, (iv) $-NH_2$ vibrations, (v) C-H, -C-N vibrations etc. It is observed that intensity of $-NH_2$; -N-H stretching vibrations gradually decrease with the decrease of PA6 content or increase of

PA12 content. It is expected, as increase of PA12 content or decrease of PA6 content causes less interplanar interaction causing a reduction in intensity of N-H stretching vibrations. Increase in concentration of 2940, 2860 cm^{-1} is also expected as PA12 content has more number of NH_2 units per unit cell than PA6.

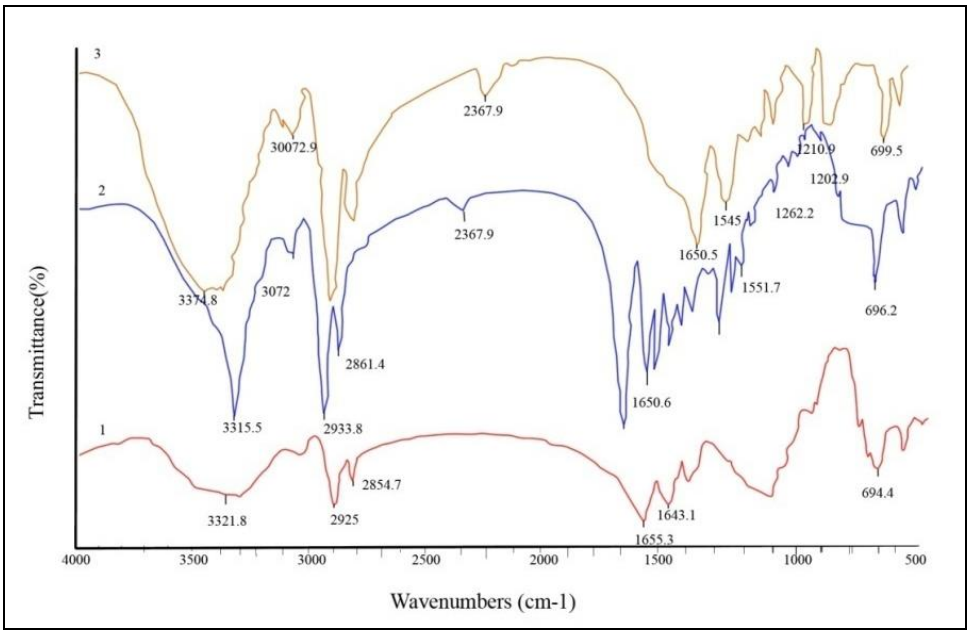

Fig. 6: *FTIR Spectra of Irradiated PA6/PA12 Copolymer with Different Compositions: Curve 1 PA6, Curve 2 5/95, and Curve 3 10/90.*

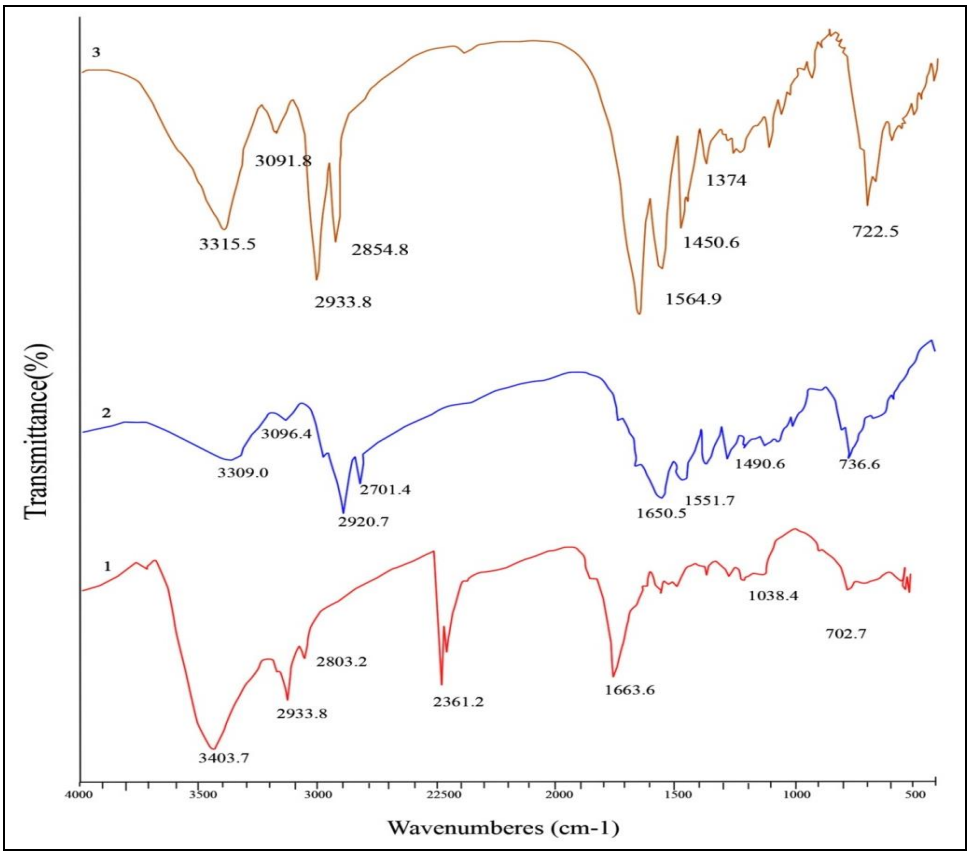

Fig. 7: *FTIR Spectra of Irradiated PA6/PA12 Copolymer with Different Compositions: Curve 1 PA6; Curve 2 5/95; Curve 3 10/90.*

CONCLUSION

Among the PA6/PA12 copolymer, hydrolyzed PA6 is observed to have more thermal stability than the copolymers. Thermal properties like T_g and T_m are formed to be more for hydrolyzed PA6 and degree of crystallinity. This is attributed to the presence of more number of intra-hydrogen bonds between the polymer chains.

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Cite this Article

Raju A, N. Mohan Babu, D. Madhuri *et al*. Spectroscopic, Thermal and Morphological Properties of PA6 Copolymers. *Research & Reviews: Journal of Physics*. 2018; 7(3): 56–62p.

