Chemical Modification of Polypyrrole. II. Thermal Stability, Dielectric, and Conductivity Characteristics of Polypyrrole Substituted with Phthalic and Pyromellitic Dianhydride

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SYNOPSIS

Polypyrrole (PPY) was electrophilically polycondensed with phthalic anhydride (PA) and pyromellitic dianhydride (PMDA). PPY–PA and PPY–PMDA polycondensates were evaluated in regard to their thermal stability and dielectric and conductivity behavior. The overall thermal stability is in the order PPY < PPY–PA < PPY–PMDA, which may be rationalized in terms of intra- and intermolecularly cross-linked structures of the polycondensates. IR spectral analyses of PPY–PA and PPY–PMDA subjected to heating at 300, 400, 500, and 550°C, respectively, were conducted to understand some of the structural changes in the polymer matrices. Both PPY–PA and PPY–PMDA exhibit high dielectric constants (200 and 125) at low frequency (10^3 Hz), which fall monotonically with increasing frequency, suggesting the possibility of interfacial polarization. The conductivity values of PPY–PA and PPY–PMDA are in the range 10^{-3}–10^{-4} ohm^{-1} cm^{-1}, which are conspicuously lower than that for unmodified PPY (2.5). This is due to the adverse effect of increasing temperature on the PPY chain stability, whereby structural conjugation and eventually conductivity will be affected. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

In continuation of syntheses and evaluation of pyrrole (PY)-based polymer systems,[1–3] Biswas and Roy described in a preceding publication[4] the preparation and structural and morphological characterization of PPY electrophilically substituted with phthalic anhydride (PA) and pyromellitic dianhydride (PMDA). This article highlights the thermal stability and dielectric and conductivity characteristics of PPY–PA and PPY–PMDA polycondensates. Although the thermal stability of PPY–PA and PPY–PMDA is appreciably enhanced, the conductivity is somewhat deteriorated relative to the unmodified PPY. At the same time, these modified polymers exhibit frequency-dependent dielectric behavior—a feature that is totally absent in the un-

modified PPY. In view of the apparent absence of any information on similar modification of PY-based polymers vis-à-vis its effect on polymer properties, the results of the present investigation may be of some significance while designing chemical modification of these polymers.

EXPERIMENTAL

The preparation of the PA- and PMDA-modified polypyrrole has been described in an earlier publication.[4] IR spectra were taken with a Perkin-Elmer 883 spectrophotometer in KBr pellets. Differential scanning calorimetry and thermogravimetric analyses were performed by a Stanton Redcroft STA 625 thermal analyzer under nitrogen atmosphere. Dielectric properties were measured by a HIOKI LCR 3530 Hitester, and conductivities, by a Kiethley 617 electrometer. The pellets were prepared under 7–8 tons of pressure and silver-coated.
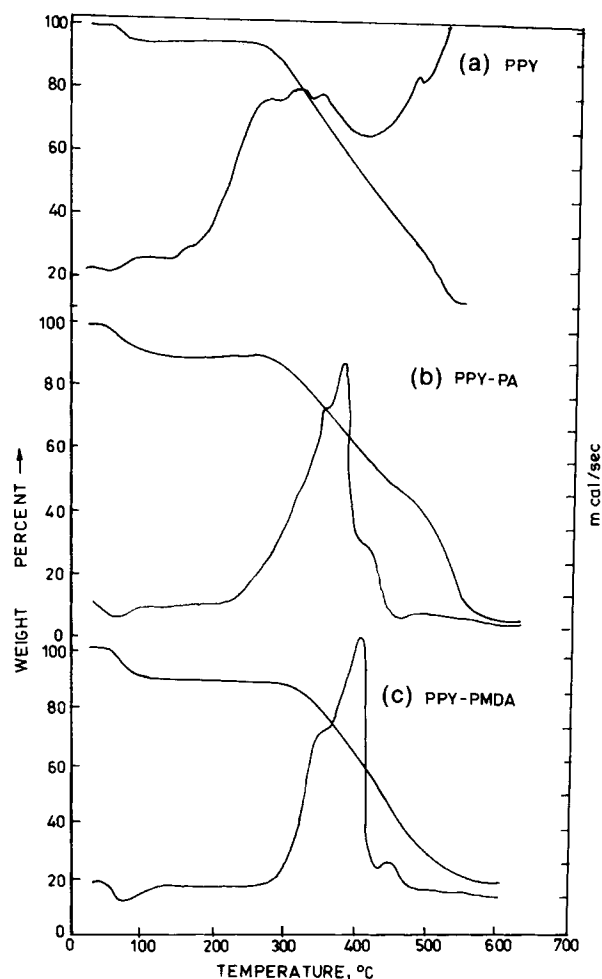

Figure 1   Thermogravimetric analysis and differential scanning calorimetric curves for (a) PPY, (b) PPY–PA, and (c) PPY–PMDA.

RESULTS AND DISCUSSION

Thermal Stability Characteristics

The thermograms of PPY, PPY–PA, and PPY–PMDA are presented in Figure 1. Temperatures for the initial decomposition (T_i) and 20, 50, and 70% decompositions are compared in Table I. These data

clearly indicate that the thermal stabilities of the anhydride-modified PPY are appreciably enhanced relative to the base polymer in the order PPY < PPY–PA < PPY–PMDA.

This trend is suggestive of a gross modification of the structure of the base polymer (PPY). According to the mechanism of the reaction of PPY with anhydrides tentatively suggested earlier[4] (Part I), PA may give rise to both intra- and intermolecularly cross-linked PPY matrix. Relevantly, carbazole,[5] poly(N-vinyl carbazole),[6] polystyrene[7] and polyacenequinone radical polymers[8] are known to afford highly thermally stable matrices upon condensation with PA and other anhydrides. Apparently, with PMDA and other multifunctional anhydrides, the possibility of the formation of a more cross-linked matrix will be higher than with PA.

Introduction of PA/PMDA moieties to PPY evidently implies the manifestation of additional C — C bonds, cyclization of the condensates, and formation of interchain cross-links. All these features will necessarily require higher thermal energy for the thermodegradation of the PPY–anhydride matrix. This should account for the general increase in the stability of the modified matrix (PPY–PA or PPY–PMDA) compared to PPY. However, the relative stabilities of these systems will also depend on the extent of possible interchain cross-linking as well as the steric constraints of the bulky anhydride moieties participating in the condensation process.

DSC analysis indicates the appearance of several exotherms in the temperature ranges 290–370°C and 420–460°C for PPY–PA and PPY–PMDA, respectively. In these temperature ranges, all these polymers seem to lose nearly 80–90% weight. Presumably, the major oxidative degradation of the polymer matrix is complete under these conditions.

IR Spectral Characteristics of Thermally Degraded PPY–PA and PPY–PMDA

Room-temperature spectra (Fig. 2 and Table II) of PPY–PA[4] show the carbonyl absorption band at

Table I   Thermal Stabilities of PPY–Anhydride-based Copolycondensates

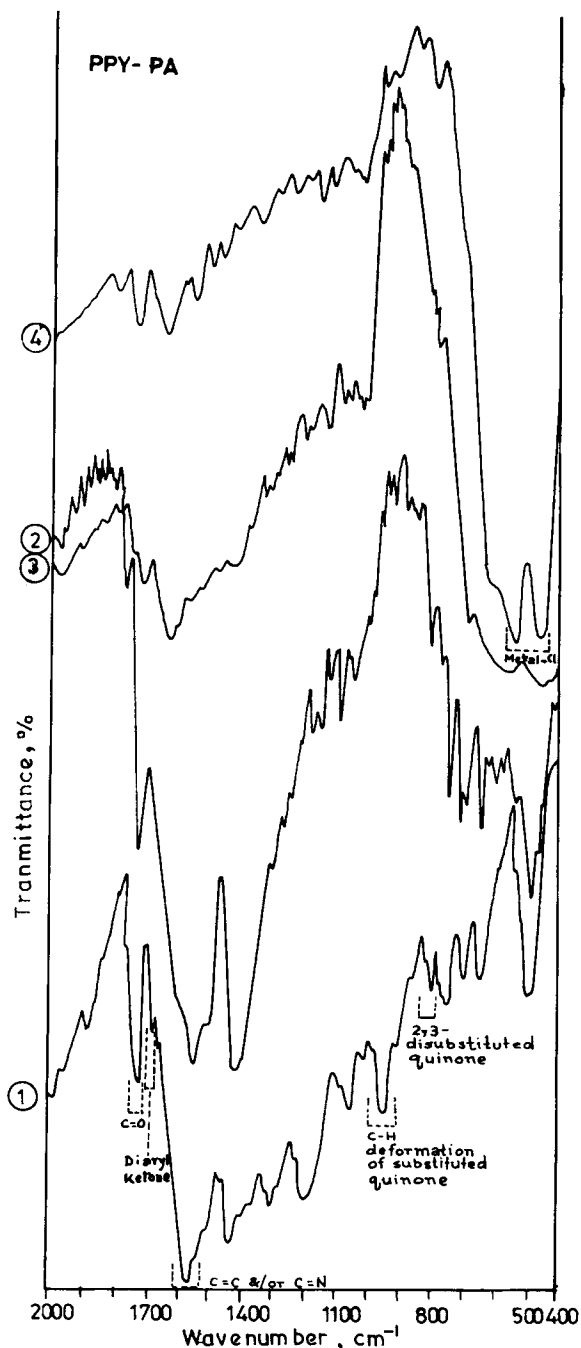| Polymer | Temperature in °C for Decomposition (%) | | | | DSC Peaks at °C | |
	Initial	20	50	70		
PPY (water)	270	331	417	524	290–370 (broad and flat)	
PPY–PA	290	351	438	554	370, 400, (small hump)	420 (small hump)
PPY–PMDA	310	364	457	572	375, 420, (flat hump)	461 (small hump)

Figure 2 IR spectra of PPY–PA: (1) at room temperature; (2) at 300°C; (3) at 400°C; (4) at 500°C.

$\sim 1698\ \mathrm{cm^{-1}}$ and another band at $\sim 1670\ \mathrm{cm^{-1}}$ due to the diaryl ketonic structure[9] (1680–1650 $\mathrm{cm^{-1}}$). PPY–PA heated at 250°C under a nitrogen atmosphere shows a similar spectrum to that of the room-temperature sample. Further heating to 300°C causes the band corresponding to the p-quinone structure to be of reduced intensity, shifting to 1716 $\mathrm{cm^{-1}}$. At this temperature, the peak at $\sim 1678\ \mathrm{cm^{-1}}$

due to the diaryl ketonic structure vanishes. At 400°C, the peaks at $\sim 1560\ \mathrm{cm^{-1}}$ for $C = C$ and/or $C = N$ stretching and $\sim 809\ \mathrm{cm^{-1}}$ for 2,3-disubstituted quinone are noted to disappear and only the peak for the p-quinone structure at $\sim 1700\ \mathrm{cm^{-1}}$ and a very weak peak at $\sim 935\ \mathrm{cm^{-1}}$ due to $C — H$ out-of-plane deformation of substituted quinone are present. At 500°C, the peak at 1720 $\mathrm{cm^{-1}}$ is present with very low intensity. At 550°C, the spectrum is similar to that of 500°C except that the peak for p-quinone structure remains at $\sim 1696\ \mathrm{cm^{-1}}$.

The room-temperature spectrum (Fig. 3 and Table II) of PPY–PMDA[4] shows two carbonyl absorption bands, one at ~ 1710 and another at $\sim 1720\ \mathrm{cm^{-1}}$, which may be assigned to the structures where (i) one anhydride group is free and (ii) both the anhydride groups are condensed. The presence of the free anhydride group is supported by the two peaks at ~ 1840 and $\sim 1763\ \mathrm{cm^{-1}}$ due to asymmetric and symmetric stretching vibrations of the two carbonyl groups of conjugated 5-membered cyclic anhydride.[9] The presence of free 5-membered cyclic anhydride is further endorsed by the $\sim 1260\ \mathrm{cm^{-1}}$ peak, corresponding to the $C — O — C$ stretching vibration.[9] PPY–PMDA heat-treated at 250°C shows a spectrum similar to that of the room-temperature sample except that the bands corresponding to the free anhydride structure, viz., ~ 1845, ~ 1762, and $\sim 1262\ \mathrm{cm^{-1}}$, are of reduced intensity, whereas the bands corresponding to the p-quinone structure are higher in intensity. At 300°C, this effect is further enhanced and the doublet peak at ~ 1720 and $\sim 1710\ \mathrm{cm^{-1}}$ merge to one peak at $\sim 1720\ \mathrm{cm^{-1}}$. On further heating to 400°C, the free anhydride peaks almost disappear, while the carbonyl peak of the p-quinone shifts to $\sim 1715\ \mathrm{cm^{-1}}$ with much reduced intensity.

One noteworthy feature is the progressive reinforcement of the peaks in the region 550–450 $\mathrm{cm^{-1}}$ in both PPY–PA and PPY–PMDA IR spectra with increasing heat-treatment temperatures (compare 1, 2, 3, and 4 in Figs. 2 and 3). The bands due to metal–halogen vibrations[9] normally occur in the region 540–220 $\mathrm{cm^{-1}}$ for $M — Cl$ stretching. The halogen atoms may act as bridging ligands between two metal atoms.[9] Bands due to both bridging and terminal halogens are observed for binuclear complexes. Tentatively, $FeCl_3$ acting as a catalyst as well as dopant in PPY synthesis and in PPY–anhydride polycondensation may give rise to these absorptions.

Dielectric Behavior

The variation of the dielectric constant (ϵ) and the dielectric loss parameters with applied frequency for

Table II IR Absorption Characteristics[a] of Heat-treated PPY–PA and PPY–PMDA

Polymer	RT		IR Absorption (cm^{-1}) of Polymers Heated to Temperature (°C)				
			250	300	400	500	550
PPY–PA	1698	(Carbonyl absorption band of p-quinone)	1713	1716	1700	1720	1696
	1670	(Diaryl ketonic absorption)	1678	—	—	—	
	1563	(C=C and/or C=N stretching)	1560	1560	—	—	
	930	(C—H out-of-plane deformation of substituted quinone)	940	926	935	—	—
	800	(2,3,-Disubstituted quinone)	790	809	—	—	—
						545	537
						472	460
PPY–PMDA	1840	(Presence of free anhydride group)	1845	1858	—	—	—
	1763	(Asymmetric and symmetric stretching vibration of carbonyl groups)	1762	1771	1773	1762	1766
	1720	(Carbonyl absorption band of p-quinone)	1719	1720	1715	1715	—
	1710		1710	—	—	—	—
	1550	(C=C and/or C=N) stretching	1553	1546	1548	—	—
	1260	(C—O—C) stretching vibration	1262	—	—	—	—
	934	(C—H out-of-plane deformation of substituted quinone)	929	931	928	923	—
	804	(2,3,-Disubstituted quinone)	800	804	813	806	—
					546	546	537
						471	461

[a] Characteristic PPY peaks have not been presented in the table.

both PPY–PA and PPY–PMDA is shown in Figure 4.

The following features are noteworthy:

(i) At low frequency (ca. 10^3 Hz), the dielectric constant for PPY–PA is ~ 200 as against ~ 125 for PPY–PMDA. Interestingly, the base polymer PPY, obtained in a water medium, shows no measurable dielectric constant in the entire frequency range of Figure 4. Furthermore, the dielectric constant values are appreciably higher compared to those for most organic materials (2–10). However, as reported by Pohl and Engelhardt,[10] the anhydride-modified polyacenequinonic polymers (PAQR) exhibit unusually high dielectric constants. Anhydride-modified poly(N-vinyl carbazole) polymers also exhibit typically high dielectric constant values at low frequencies.[5]

(ii) The dielectric constants of both PPY–PA and PPY–PMDA fall monotonically with increasing applied frequency to a limiting value (20–40 at 10^6 Hz).

(iii) For both PPY–PA and PPY–PMDA, the dielectric loss parameter (tan δ) falls mono-

tonically with applied frequency, a feature atypical of a broad[11] relaxation.

The observed dielectric constant frequency pattern, which is quite similar to that exhibited by other anhydride-modified polymer systems reported by Biswas et al.,[5–7] suggests that dipole orientation is restricted by the cross-linked polymer matrix presenting heavy frictional damping on the dipole rotation. As a result, its response to the applied field will be of the relaxation type, the rotation falling further and further in the phase behind the applied field. Consistent with the dielectric-frequency behavior, the variation of tan δ with the applied frequency is atypical of a broad relaxation, being otherwise featureless in regard to any dipole group loss and related phenomena.

The high dielectric constant values (~ 200) in the low-frequency (10^3 Hz) region deserve some comments. Relevantly, similar high dielectric values have been also noted by Biswas et al. for poly(N-vinyl carbazole)-1,4,5,8-naphthalene tetracarboxylic dianhydride[5] polycondensate (~ 90) and for anthracene-co-anthracene polysulfones (~ 100; 10^4 Hz). So far, the most unusually high dielectric con-
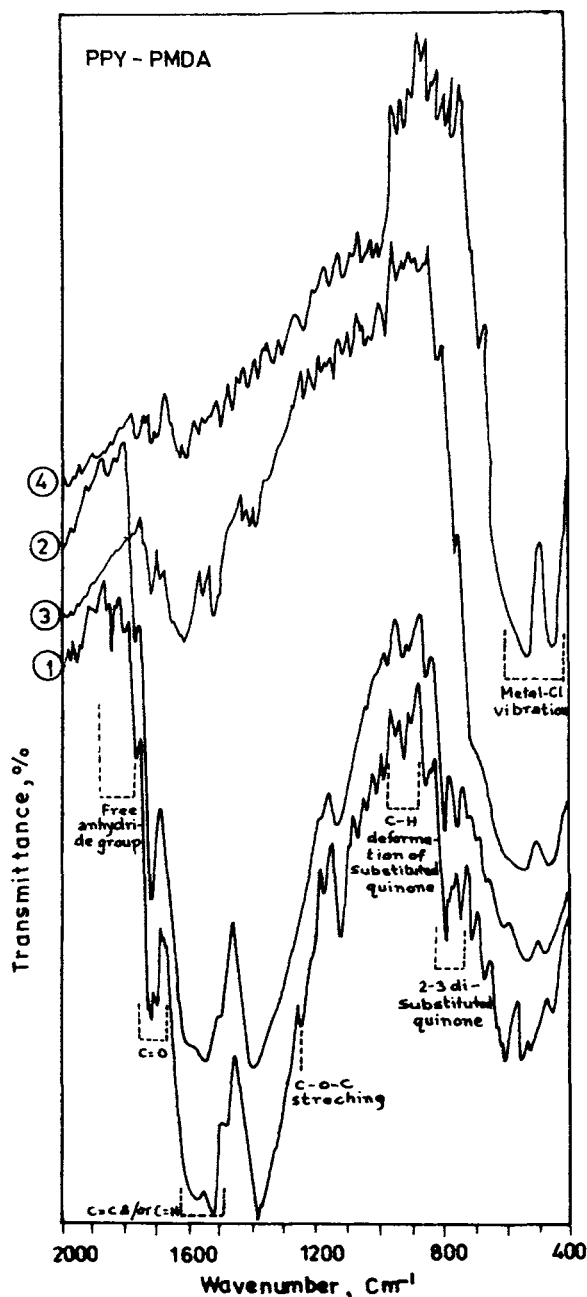
interfacial polarization decreases with increasing frequency.[11] Evidently, such a situation is likely to prevail in the polycondensates of the types discussed in the present context and the cited cases.

Conductivity Characteristics

Table III presents the conductivity values for PPY, PPY–PA, and PPY–PMDA realized under various experimental conditions. Unmodified PPY prepared in water with the $FeCl_3$ catalyst exhibits the highest conductivity value as reported earlier.[3] However, the conductivity is found to decrease upon anhydride modification. In contrast to this behavior, Biswas and Mitra reported an appreciable enhancement in conductivity for PNVC ($\sim 10^{-16} ohm^{-1} cm^{-1}$) upon modification[5] with various aromatic anhydrides ($\sim 10^{-5}$–$10^{-7} ohm^{-1} cm^{-1}$). From the structural point of view also, additional conjugated structures in modified PPY should have an implied enhancement of conductivity.

A possible explanation for the observed fall in conductivity in PPY–PA or PPY–PMDA may be offered by considering the adverse effect of high temperature on the inherent stability of the PPY backbone vis-à-vis the conductivity of PPY. The data of Table III distinctly suggest that under iso-
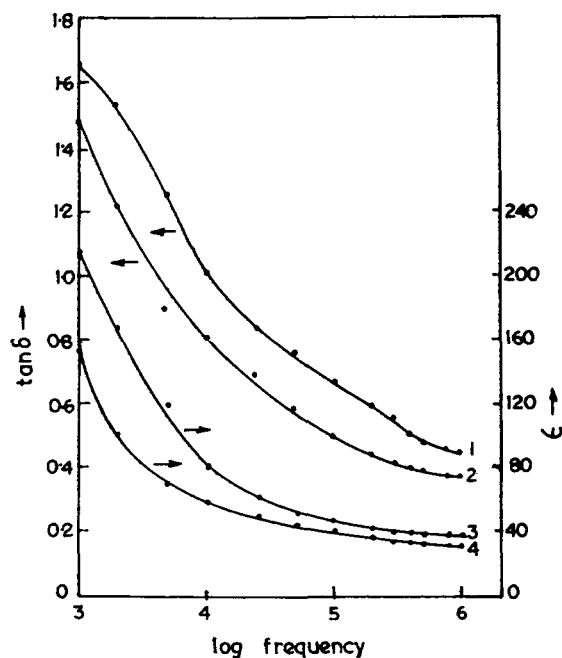

Figure 3 IR spectra of PPY–PMDA: (1) at room temperature; (2) at 300°C; (3) at 400°C; (4) at 500°C.

stant values have been realized with the PAQR polymers ($\sim$ 900 at 300 Hz) by Pohl and co-workers.[12]

It is commonly believed that such high dielectric constants at low frequencies originate from interfacial polarization in polymers having structural inhomogeneity between materials of different dielectric constants and conductivities. Characteristically,

Figure 4 Dielectric constant (ϵ) and dielectric loss (tan δ) vs. log frequency plots of the polycondensates: (1) PPY–PA; (2) PPY–PMDA.

Table III   Dc Conductivities of the PPY–Anhydride-modified Copolycondensates

Polymer	Preparation Condition	Pretreatment Condition PPY Heated at 200°C (h)[a]	Conductivity (ohm^{-1} cm^{-1})
1. PPY	PY : FeCl$_3$	—	2.46
	1 : 4 (mole ratio)	1 (80)	1.08
		2	2.5×10^{-1}
		4 (73)	3.5×10^{-2}
		6	2×10^{-3}
		8 (70)	6×10^{-4}
		10 (69)	1.5×10^{-4}
2. PPY–PA	PPY : PA : ZnCl$_2$	—	1.01×10^{-3}
	1 : 3 : 5 (wt ratio)		
3. PPY–PA	PPY : PA : FeCl$_3$	—	4.89×10^{-3}
	1: 3 : 5 (wt ratio)		3.85×10^{-3}
4. PPY–PA	PPY : PA : FeCl$_3$	—	6.32×10^{-3}
	1 : 6 : 5 (wt ratio)		
5. PYY–PMDA	PPY : PMDA : FeCl$_3$	—	3.5×10^{-4}
	1 : 1 : 5 (wt ratio)		
6. PPY–PMDA	PPY : PMDA : FeCl$_3$	—	5.22×10^{-4}
	1 : 3 : 5 (wt ratio)		
7. PPY–PMDA	PPY : PMDA : FeCl$_3$	—	7.2×10^{-4}
	1 : 6 : 5		
8. PPY–PMDA	PPY : PMDA : FeCl$_3$	—	1.4×10^{-3}
	3 : 1 : 5		

[a] Figures in parentheses indicate % weight residue remaining.

thermal heating condition at 200°C PPY progressively loses its conductivity with time of heating. The synthesis of PPY–PA or PPY–PMDA required exposure at elevated temperatures for prolonged periods (160 ± 10°C, 250 ± 10°C, 8 h); under these conditions, the conductivity of the base polymer (PPY) is seen (Table III) to fall from ~ 3 ohm^{-1} cm^{-1} to ca. 10^{-4} ohm^{-1} cm^{-1}. Significantly, compared to this value, the PA-modified PPY shows somewhat improved conductivity, depending upon the preparation conditions employed (Table II).

Several reports are available in the literature corroborating the adverse effect of temperature on PPY conductivity. Thus, Street et al.[13] reported an irreversible decrease in the conductivity of the PPY–tetrafluoroborate system beyond 150°C even in helium. Salmon et al.[14] also observed that, in PPY doped with perchlorate, hexafluorophosphate lost conductivity and decomposed at ca. > 150°C in air. Further, Samuelson and Druy[15] reported the degradation of the conductivity of PPY/toluene sulfonate to obey first-order reaction kinetics, whereas other dopants followed a multiorder kinetics.

The most probable reason for the observed decrease in conductivity with increasing temperature appears to be due to the structural damage caused

in the PPY matrix exposed to isothermal heating at elevated temperature. Thus, in run no. 1 of Table III, the figures in parentheses of column 3 indicate a loss in the weight of the residue. Such thermal degradation of the PPY chain will evidently affect its conjugated structure and, hence, the conductivity. Further, the conductivity losses observed in the present case are irreversible, which also implies permanent damage in the original structure of the conducting PPY matrix.

Table III further reveals that conductivities tend to increase progressively as the PA/PMDA amount increases in the initial feed composition. Relevantly, with higher amounts of PPY in the feed relative to PMDA (3 : 1 wt ratio, Table III, no. 8), the highest conductivity has been realized with the PPY–PMDA system.

A further feature of interest is that prepared with comparable feed ratios: PPY–PA condensates exhibit about one order higher conductivity than that of the PPY–PMDA condensates. This difference may result from the possibility of a lesser extent of polycondensation involving bulkier PMDA moieties than with the PA moieties, which will imply a lesser extent of conjugation and eventually lower conductivity.

CONCLUSION

The polycondensation of polypyrrole with phthalic anhydride and pyromellitic dianhydride yields materials that show enhanced thermal stability and frequency-dependent dielectric constants and high loss parameters, but inferior conductivity characteristics.

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