Synthesis, Characterization, and Kinetic Study on the Thermal Decomposition of Polyamidoethers

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Synopsis

Some new polyamidoethers have been synthesized by condensation reaction of N, N'-dichloro-acetyl-1,4-phenylene-diamine with bisphenols (4,4'-isopropylidenediphenol, 4,4'-dihydroxydi-phenyl sulfone, 4,4'-dihydroxydiphenyl sulfide, and 4,4'-dihydroxybiphenyl) in N-methylpyrroli-done medium using DB-24-Crown-8 as a phase-transfer catalyst. The structure of these polymers has been characterized by infrared (i.r.) and ^{1}H nuclear magnetic resonance (NMR) spectroscopy. Kinetic method of thermal decomposition of these polymers and their 2% mixture with polyvinylchloride (PVC) has been studied.

INTRODUCTION

Polyamidoethers are known for their high thermal and other desirable physical and mechanical properties.[1-3] Various monomers have been reported in the synthesis of polyamidoethers,[4,5] including the polycondensing N, N'-dichloroacetyl-O-dianisidine with various dihydroxyarene, and aliphatic diols.[6] In polymer chemistry, phase-transfer catalyst (PTC) was effectively exploited in anionic addition and condensation polymerization,[7] and more recently the use of solid–liquid PTC to effect polycondensation.[8]

We have reported aromatic nucleophilic substitution polymerization using PTC under mild conditions, leading to the formation of aromatic polyethers.[9] As a continuation of this study, we have successfully prepared aromatic polyamidoethers by the polymerization of N, N'-dichloroacetyl-1,4-phenyl-enediamine with various dihydroxyarenes.

EXPERIMENTAL

Materials

All solvents were reagent grade. Bisphenol-A (4,4'-isopropylidendiphenol) and 4,4'-thiodiphenol (TDP) were recrystallized twice from toluene; 4,4'-sulfonyldiphenol (SDP) was recrystallized twice from a benzene/ethanol mixture, 4,4'-dihydroxydiphenyl (Riedel) was used as received. DB-24-Crown-8 (Fluka) was used without further purification. N, N'-dichloroacetyl-1,4-phen-ylenediamine (N, N'-DCPDA) was prepared as described.[9c]

Polymerization Method

To a solution of 5.18 mmol of N, N'-DCPDA and 5.18 mmol of the appropriate bisphenol in 20 mL of N-methylpyrrolidone (NMP) was added

22.4 mmol anhydrous K_2CO_3 and 1.41 mmol of DB-24-Crown-8 in a 100-mL flask, equipped with an N_2 inlet, a water-cooled condenser, and a thermometer. After stirring for 24 h at 88°C, the mixture was cooled and slowly poured into 150 mL methanol. The polymer was then filtered off. This solid was worked up by boiling three times for 1 h with 150 mL methanol and then three times for 1 h with 150 mL water. Finally, the powder was soxhlet-extracted overnight with methanol-acetone (90 : 10). The product was dried overnight at 120°C to render the polymers.
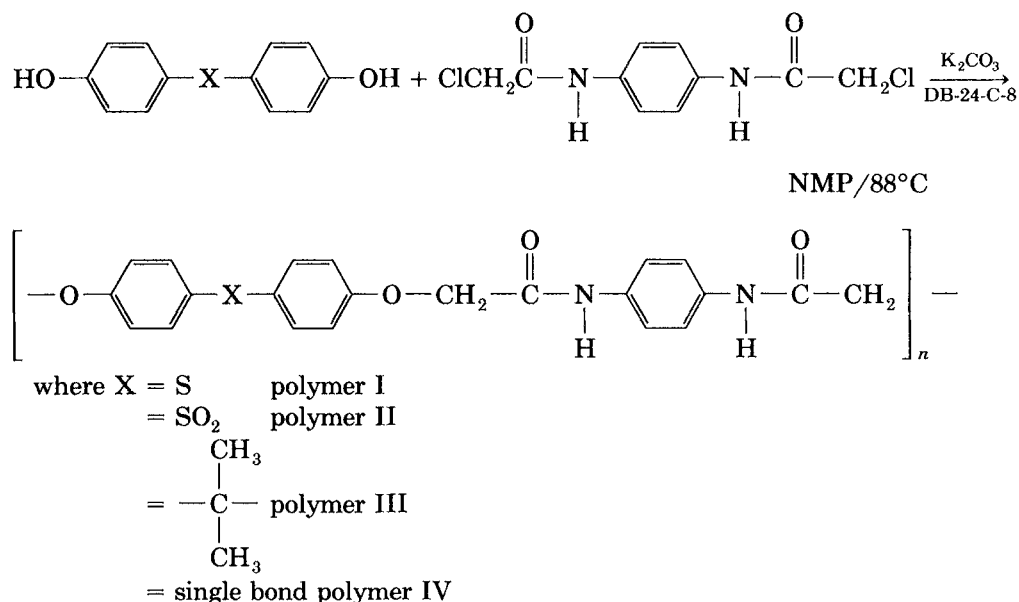
Measurements

Infrared (IR) spectra of polyamidoether samples were scanned in KBr pellets on a Pye-Unicam SP-1000 Infrared spectrophotometer.

^{1}H-NMR analysis. Spectra were obtained on a Varian Associates EM-390 90 MHz NMR spectrometer. CD_3SOCD_3 was used as an internal standard. TMS was used as an external standard.

Thermal properties. Thermal behavior was examined using TG 760 series of Stanton Redcroft thermogravimetric analyzer from room temperature to 550°C at a heating rate of 5°/min in N_2 atmosphere.

RESULTS AND DISCUSSION

Several polyamidoethers were synthesized by condensation polymerization of N,N'-dichloroacetyl-1,4-phenylenediamine with a number of bisphenols in N-methylpyrrolidone (NMP) at reflux temperature (88°C) using DB-24-Crown-8 as the phase-transfer catalyst. The overall reaction scheme is given below.

where X = S   polymer I
    = SO_2 polymer II

$$= -\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}- \text{ polymer III}$$

    = single bond polymer IV

The structure of these polyamidoethers was confirmed by the IR spectra. Comparison of IR spectra of the monomers N,N'-dichloroacetyl-1,4-phenylenediamine and bisphenols and their polymers (Table I) were obtained to show

TABLE I
Assignment of Characteristic Frequencies in IR Spectra

Compound	Wavenumber (cm^{-1})	Intensity	Assignment
N, N-dichloroacetyl-	735, 750	S	C—Cl
1,4-phenylenediamine	1675	VS	C=O
	965	M	Due to crystallinity
	3100	S, Sh	N—H
	3175	S, Sh	N—H
	3265	S, b	N—H
Polymers I, II, III,	1060–1065	S	C—O—C
and IV	1235–1250	VS	C—O—C
	1680–1690	VS	C=O
	3000–3500	S, b	N—H
	2960	W, Sh	$\begin{array}{c} CH_3 \\ \mid \\ -C- \\ \mid \\ CH_3 \end{array}$
	1360, 1380	VW, b	$\begin{array}{c} CH_3 \\ \mid \\ -C-\text{geminal} \\ / \\ CH_3 \end{array}$
	1150, 1310	VS	SO_2
	680, 720	W	C—S

Where: Sh = sharp; b = broad; S = strong; W = weak; m = medium; VW = very weak; VS = very strong.

that the bonds at 735 and 750 cm^{-1} due to the C—Cl stretching vibration in the monomer have disappeared. The IR spectra exhibited characteristic absorptions at 1060–1065 cm^{-1} and 1235–1250 cm^{-1} due to (C—O—C) stretching. The medium absorption band at 965 cm^{-1} has been observed in the N, N'-dichloroacetyl-1,4-phenylenediamine monomer, but disappears after polymerization process. This band might possibly be attributed to the crystallinity.[10]

The formation of ether bonds in the polymers was best demonstrated by using ^{1}H-NMR. The chemical shifts of all the polyamidoethers (I, II, III) are tabulated in (Table II). Assignment was made by comparing the spectrum of the polyamidoethers. For polymer III the chemical shift at (5.18–5.6) δ is assigned to the CH_2 protons and the chemical shift at 6δ is assigned to the N—H proton. While in polymers I and II, the positions of chemical shifts of CH_2 and N—H protons are changed in comparison with polymer III. These differences in chemical shifts might presumably be due to the effect of the (X = S, SO_2) group. Thermal gravimetric analysis (TGA)-thermogram of pure polyamidoethers is shown in Figure 1. The DTG curve indicates that the polyamidoethers (I, II, III, IV) degrade in one stage. These polymers start to lose weight between 270–280°C. The rate of weight loss became very rapid after the heating temperature exceeded 325°C.

TG of pure PVC and PVC mixed with 2% different polyamidoethers (I, II, III, IV) at temperatures from 0 to 550°C in N_2 atmosphere are also

TABLE II
Assignment of Characteristic Chemical Shifts in ^{1}H-NMR Spectra[a,b]

Compound	Chemical shifts of aromatic proton, δ(ppm)	Chemical shifts of aliphatic proton, δ(ppm)
Polymer in CD_3SOCD_3	7.52–7.72 (2H, m, aromatic)	4.54–4.9 (2H, m, 2NH)
I	6.84–7.42 (10H, m, aromatic)	3.42 (4H, 2CH$_2$, d, J = 7.5 Hz)
II	8.0–8.7 (4H, m, aromatic)	4.8 (2H, S, 2NH)
	7.42–7.64 (4H, m, aromatic)	3.33 (4H, 2CH$_2$, d, J =
	7.02–7.32 (4H, m, aromatic)	5H$_z$)
III	8.34–8.6 (4H, m, aromatic)	6.0 (2H, S, 2Me)
	7.92–8.2 (4H, m, aromatic)	3.03 (6H, S, 2Me)
	7.2–7.7 (4H, m, aromatic)	5.18–5.6 (4H, m, 2CH$_2$)
IV	Insoluble in deutrated solvent	

[a] The spectra are consistent with the expected structure although some impurities are present.
[b] Monomer N,N'-dichloroacetyl-1,4-phenylenediamine is insoluble in deutrated solvent.
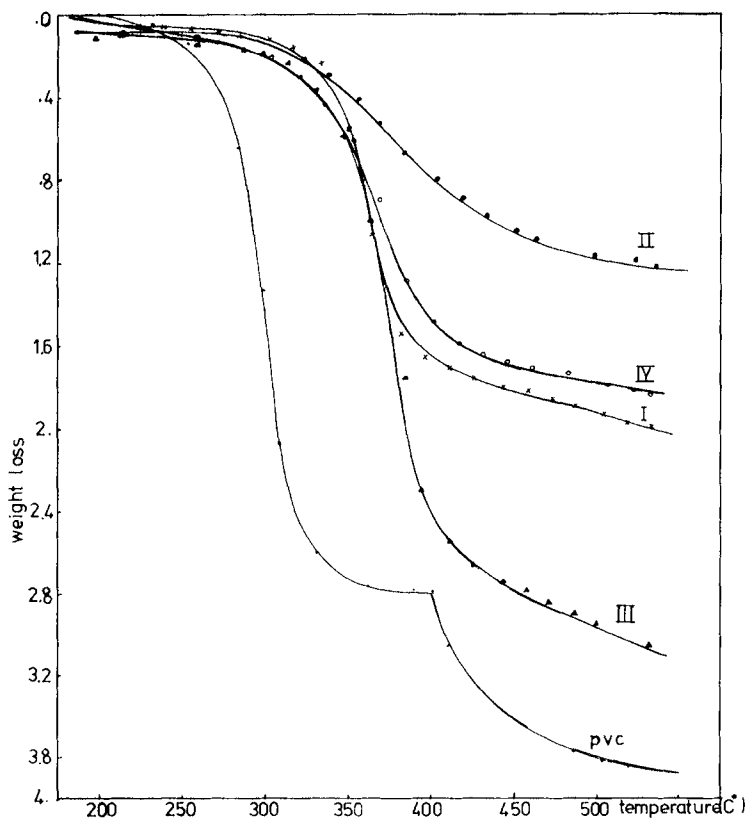

Fig. 1.   TG analysis of pure PVC and polymer samples (I, II, III, IV).
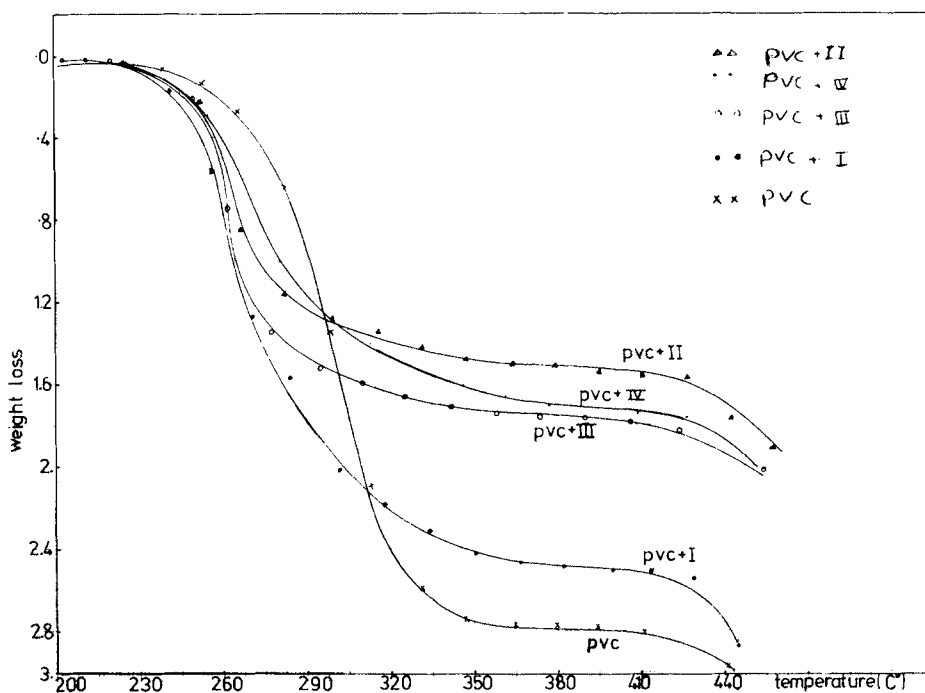
Fig. 2.   TG analysis of pure PVC and PVC mixed with 2 wt% of polymer samples (I, II, III, IV).

recorded as shown in Figure 2. The results of this degradation have shown that the thermal stability of PVC was increased by added polyamidoethers. The method of Anderson and Freeman was applied for kinetic study of thermal degradation of pure polyamidoether, pure PVC and PVC mixed with 2% of different polyamidoethers.[11] Activation energies and order of reactions (Table III) were calculated from the Anderson and Freeman equation after plotting $\Delta \ln(dw/dT)$ against $\Delta \ln W_r$ at constant $\Delta(1/T)$. The plot yields

TABLE III

Kinetics Parameters for the Decomposition of Pure PVC, Pure Polyamidoethers and PVC mixed with 2% of Polyamidoethers at Different Temperatures from 0°C to 550°C in N_2 Atmosphere at Heating Rate of 5 min/°C

Compound	Activation energy (kcal/mol)	Order of reaction (n)
Pure PVC	28.6	1.091
Pure polyamidoether		
I	46.20	0.956
II	33.28	2.00
III	27.82	0.933
IV	34.97	1.000
PVC with 2% polymer		
I	44.71	1.88
II	52.29	2.286
III	39.94	2.0456
IV	41.73	2.197

E/R as the intercept and tangent of the slope as order of reaction.

$$\Delta \ln\left(\frac{dw}{dT}\right) = n\Delta \ln W_r - \left(\frac{E}{R}\right)\Delta\left(\frac{1}{T}\right)$$

where dw/dT = reaction rate

n = order of decomposition
$W_r = \Delta W_c - \Delta w$ = weight of remaining sample
Δw = weight loss at the point where dw/dT is taken
ΔW_c = total weight loss associated with a given reaction
E = activation energy

From the result of calculated activation energies, it was found that the order of thermal degradation of pure polyamidoethers decreased as follow

I > IV > II > III

whereas the order of thermal stability of PVC mixed with 2% of polyamidoethers decreased according to the following order.

II > I > IV > III

This is in agreement with the degradation of pure polyamidoethers (I, IV, III), but in the case of polymer II, the situation is different. It is obvious from previous works[12] that the presence of the SO_2 group in the polymer clearly shows considerably more thermal stability than the other polymers. This evidence is quite consistent with the increases of thermal stability of PVC by polymer II and this reaction compared to the thermal degradation of pure polymer II might operate according to in different mechanisms, which may act in various ways to stabilize PVC either by reaction with proton donor-evolved HCl[13] or ionic or by free radical reactions.[14] For thermal degradation of pure polymer II, the lower stability of this polymer might be due to the presence of SO_2 group together with the acidic amido proton. The SO_2 group acts as a base to extract hydrogen from the amido group which is then rearranged and followed by desulfonation to give another product similar to that produced by high temperature (375–400°C) on the conversion of *bis*-(2,4,6-trimethylphenyl) sulfone to the 2,4,6,3′,5′-pentamethyldiphenyl-methane.[15]

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