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SYNTHESIS AND CHARACTERIZATION OF NEW POLYETHERAMIDES

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ABSTRACT

Polyetheramides (PEAs) are prepared by polycondensation of *N,N'*-diacetyl-*o*-tolidide with Bisphenol A, C, or F, phenolphthalein, resorcinol, catechol, hydroquinone, or 1,5- or 2,7-dihydroxynaphthalene or ethylene, butylene, propylene, diethylene, or triethylene glycol. The fusible and soluble oligomers are characterized. An attempt is made to bring out the relationship between various properties of PEAs and their structures.

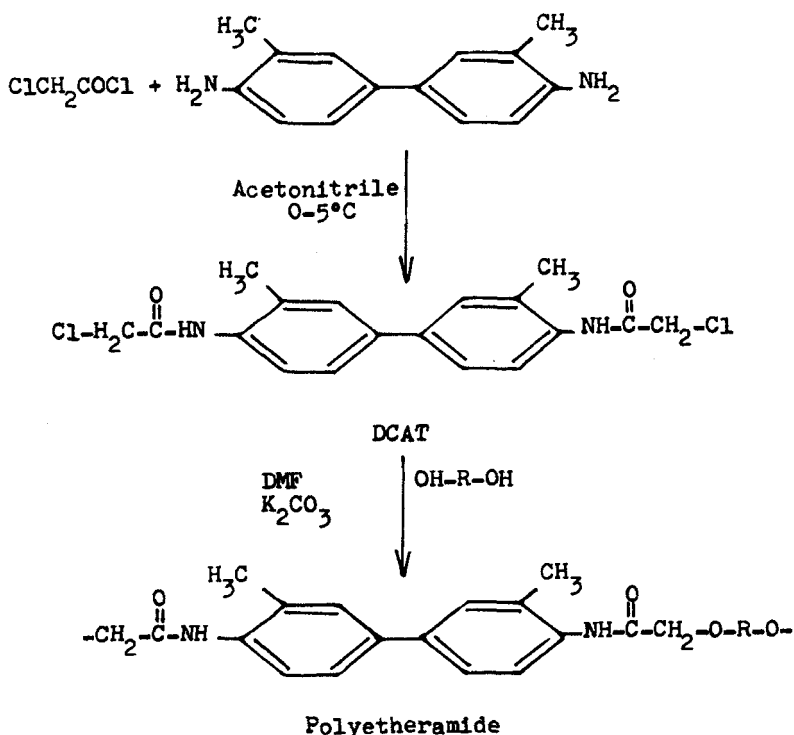
INTRODUCTION

The presence of aromatic rings in the backbone chain of the polyamides enhances their mechanical and heat-resistant properties at the cost of their melt and/or solution processability [1, 2]. The latter characteristics are improved by the introduction of an ether bridge in their backbone [3, 4]. The degree of improvement is much enhanced if the methylene bridges are introduced in the backbone along with ether bridges [5]. The polyetheramides have been reported to be useful as matrix resins for composites [5-7]; the resultant composites have good mechanical and thermal properties with better chemical resistance [6]. The polyetheramides reported in the present communication were synthesized by polycondensation of a bisamidodichloride,

TABLE 1. The Characteristics of PEA Samples from DCAT and OH-R-OH

PEA sample no.	OH-R-OH	Softening range, ^a °C	$[\eta] \times 10^3$ ^b dL/g	\bar{M}_n by VPO
1	Bisphenol A (BA)	160-175	74	2000
2	Bisphenol F (BF)	166-180	78	2000
3	Bisphenol C (BC)	110-125	73	1850
4	Phenolphthalein (PHE)	168-190	72	1600
5	Resorcinol (RSO)	146-160	96	1800
6	Hydroquinone (HYO)	160-175	93	1750
7	Catechol (CAO)	135-145	98	1750
8	2,7-Dihydroxynaphthalene (2,7-NA)	170-185	78	1700
9	1,5-Dihydroxynaphthalene (1,5-NA)	105-125	74	1700
10	HO(CH ₂) ₂ OH (EG)	210-220	150	1800
11	HO(CH ₂) ₂ O(CH ₂) ₂ OH (DEG)	206-216	125	1750
12	HO(CH ₂ CH ₂ O) ₂ (CH ₂) ₂ OH (TEG)	185-200	103	1750
13	HO(CH ₂) ₂ OH (PG)	200-205	98	1700
14	HO(CH ₂) ₄ OH (BG)	1900-200	88	1800

^aUncorrected capillary softening temperatures.^bAt 35°C in dioxane.



SCHEME 1.

viz., *N,N'*-dichloroacetyl-4,4'-diamino-3,3'-dimethylbiphenyl (*N,N'*-dichloroacetyl-*o*-tolidide, DCAT) with various diols (Table 1). A typical reaction is shown in Scheme 1.

All the polyetheramides (PEA) were synthesized under the optimum reaction conditions to obtain soluble and fusible products, and the polyetheramide samples were characterized.

EXPERIMENTAL

Materials

All the chemicals and solvents employed for the synthesis of polyetheramides were of L.R. Grade. Bisphenol C and F were prepared by a reported

method [8]. The solvents used for characterization of PEA samples were purified by distillation.

Monomer Synthesis

Synthesis of *N,N'*-Dichloroacetyl-*o*-tolidide (DCAT)

A cooled mixture of chloroacetyl chloride (1.23 g, 0.011 mol) in acetonitrile (50 mL) was added dropwise with stirring to a well-cooled solution of *o*-tolidine (1.92 g, 0.01 mol) in acetonitrile (200 mL) over 1 h at a temperature below 5°C. A solution of sodium bicarbonate (10%) was added dropwise with stirring till the product separated out. The solid was filtered and washed successively with 10% aqueous HCl and boiling water. The air-dried DCAT was crystallized from methyl ethyl ketone; mp 216-217°C.

The IR spectrum of the product exhibited a carbonyl band at 1705 cm⁻¹.

Analysis. Calculated for C₁₈H₁₈O₂N₂Cl₂: N, 7.67%; Cl, 19.45%. Found: N, 7.3%; Cl, 18.6%.

Polycondensation of DCAT with Bisphenol A (BA) in the Presence of K₂CO₃ in DMF

To a well-stirred solution of DCAT (3.64 g, 0.01 mol) in DMF (3 mL), potassium carbonate (2 g) and Bisphenol A (2.68 g, 0.01 mol) were added. After standing for 1 h, the reaction mixture was refluxed at 155°C for 6 h. The thick liquid was stirred into 10% aqueous HCl (200 mL). The solid product which separated out was filtered off, washed twice with boiling water, and dried in air. The polyetheramide sample, DCAT-BA, was obtained in 68% yield. It melted over a temperature range of 160 to 175°C.

All the other PEA samples listed in Table 1 were synthesized by the same procedure.

MEASUREMENTS

IR spectra of the PEA samples in KBr were scanned on a Perkin-Elmer spectrophotometer. UV spectral analysis of PEA samples in DMF were obtained with a 220-S-Hitachi spectrophotometer.

The thermogravimetric analysis (TGA) of PEA samples was carried out with a Du Pont 951 thermogravimetric analyzer in air at a heating rate of 10°C/min. Viscometric measurements were done on DMF solutions with an Ubbelohde suspended-level viscometer at 35 ± 0.1°C.

The number-average molecular weights were estimated by vapor-pressure osmometry with DMF as solvent at 70°C. The osmometer was calibrated using benzil.

RESULTS AND DISCUSSION

The reaction of DCAT with Bisphenol A (BA) was carried out under various conditions to establish optimum conditions. It was observed that polycondensation at melt temperature in the presence of K_2CO_3 afforded an insoluble and infusible mass. Pyridine and triethylamine could not bring about polycondensation. The polycondensation in nitrobenzene at 200°C yielded an insoluble and infusible product. The polycondensation in DMF at 150°C for 6 h in the presence of K_2CO_3 afforded a soluble and fusible product of fairly high intrinsic viscosity. Hence the polycondensation of DCAT with other diols was effected under these conditions. The molecular weights of these PEA samples, reported in Table 1, are low, i.e., these PEA samples are oligomers.

The PEA samples obtained by condensing DCAT with various aliphatic diols were dark in color. Those prepared from aliphatic diols have lower solubility in DMF and DMSO than those from various dihydroxyarenes listed in Table 1. All the PEA samples were insoluble in other common organic solvents.

All the PEA samples showed the expected IR absorptions: secondary $-NH-$ stretching extending from 3 500 to 3 000 cm^{-1} , with a maximum at around 3 400 cm^{-1} ; the $C=O$ band at 1 705 cm^{-1} ; a strong $C-O-C$ band at 1 235 cm^{-1} ; and strong bands at 820 and 860 cm^{-1} . UV absorption spectra of dilute solution of PEAs (0.7 mmol/L in DMF) prepared from aliphatic diols showed characteristic absorption maxima around 275 nm and those prepared from dihydroxyarenes showed absorption maxima around 285 nm.

The PEAs obtained from aliphatic diols had comparatively lower solubility, higher softening temperature, and higher intrinsic viscosity than PEAs prepared from dihydroxyarenes. It can be seen that there is not much difference in the average degree of polymerization of PEA samples. The property difference may be attributed to the difference in the bulkiness of the polymer chains. In the PEAs prepared from dihydroxyarenes, the bulk of the polymer chains is comparatively high. This will prevent the close approach of the polymer chains and thereby will reduce intermolecular H bonding. In case of PEAs obtained from aliphatic diols, the reverse situation obtains, favoring a comparatively closer approach of polymer chains and higher

intermolecular H bonding. This would explain, on a broad basis, the differences in solubility, softening temperature range, and intrinsic viscosity of dilute solution of these two types of PEA.

The PEAs obtained from aliphatic diols can be divided into two groups: those obtained from ethylene, propylene, and butylene glycols, and those obtained from ethylene, diethylene, and triethylene glycols. In both series the softening range decreases in the stated order. This suggests that the softening range decreases with increasing size of the bridge.

In order to decide the trend in the thermal stability, TGA parameters such as T_0 (initial decomposition temperature), T_{10} (temperature for 10% weight loss), and T_m (temperature for maximum rate of decomposition) were calculated [9, 10]. In order to get a more quantitative picture of the relative stability of PEA sample, the IPDTs (integral procedure decomposition temperature) were calculated [9]. The IPDT represents the overall nature of TG thermogram over the entire range of the TGA [10]. The ultimate weight loss was measured at 700°C.

Examination of the TGA data in Table 2 reveals that the PEA samples can be divided into two groups: Samples 10 to 14, prepared from aliphatic diols, and Samples 1 to 9, prepared from dihydroxyarenes. Accepting T_0 , T_{10} , T_m , or IPDT as the criterion of relative thermal stability, the samples from aliphatic diols can be ranked as thermally more stable than those from dihydroxyarenes. However, in view of the uncertainty in the IPDT ($\pm 20^\circ$), it is difficult to be sure about the relative thermal stability of these two groups.

It has been observed that the thermal stability of polyamides is affected most by the structure of the diamine in it. In our case the amide structure is common in all the products. The variation in the thermal stability will, therefore, be mainly due to difference in the structure of the $-R-$ moiety of the $-O-R-O-$ bridges. As indicated above, the hindrance to the closer approach of the PEA molecules prepared from dihydroxyarenes weakens the intermolecular interactions of such PEA samples. The same features seem to determine the difference in the thermal stability of the PEA samples prepared from aliphatic diols and dihydroxyarenes.

The TGA data were analyzed by the method developed by Reich and co-workers [11] to estimate the order and energy of activation of the overall degradation reaction. The results revealed that the degradation from 10% to nearly 90% follows first-order kinetics with energies of activation from 150 to 200 kJ/mol.

TABLE 2. Thermal Characteristics of PEA Samples

PEA sample no.	T_0 , °C	T_{10} , °C	T_m , °C	IPDT, °C	E , kJ/mol
1	280	300	530	527	187
2	295	310	540	538	179
3	275	285	530	527	196
4	270	285	520	510	192
5	295	300	520	507	158
6	300	315	509	500	163
7	300	315	540	535	158
8	270	300	530	520	154
9	275	286	540	535	150
10	210	330	610	603	158
11	315	328	630	620	175
12	330	338	650	642	200
13	345	350	640	628	200
14	340	348	600	595	175

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