Polyethers. I. Polyethers from 2,4-Dichloroquinolines and Alkylene Diols

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Synopsis

Polyethers are prepared by condensing, respectively, 2,4-dichloroquinoline and its 6-methyl and 6-methoxy derivatives separately with ethylene, propylene, butylene, diethylene and triethylene glycols. These polyethers are characterized and the electrical conductivity of polyethers is measured at various temperatures up to 150°C.

INTRODUCTION

The polyethers are known to possess the quality of chemical resistance of ethers.[1] Some polyethers have attained high industrial importance due to their all round applications and more particularly due to their certain characteristics which are lacking in other engineering plastics.[2-4] Except polyethers ETO, PRO, ECH, polyoxymethylene and poly(2,6-dimethylphenylene oxide),[5] other polyethers may be prepared by polycondensation of appropriate dihalide monomer and the required dihydroxy compound.[6] Most of these dihalides have a structure of the type $Cl—CH_2—R—CH_2—Cl$. It is reported that dichloro-aza-heterocycles containing the chlorine atoms in 2 and 4 positions with respect to ring-nitrogen atom are reactive. The easily obtainable dichloro-aza-heterocycle is 2,4-dichloroquinoline (DCQ). It is reported that DCQ reacts with an ethoxide affording 2,4-diethoxyquinoline if the reaction conditions are vigorous.[7] This suggested that a DCQ on reaction with a diol or a dioxide would afford polyethers. With a view to examining this possibility the work presented herein dealing with polycondensation, respectively, of DCQ and its 6-methyl and 6-methoxy derivatives separately with five diols listed in Table I, was undertaken. These polyethers are characterized.

EXPERIMENTAL

2,4-Dichloroquinoline (DCQ), 6-methoxy-2,4-dichloroquinoline (6-MeO-DCQ), and 6-methyl-2,4-dichloroquinoline (6-Me-DCQ) were prepared by reported methods.[8-10] The five glycol monomers were laboratory-grade reagents. The glycoloxides were prepared by treating the required glycol with sodium.

It was observed that condensation of each DCQ with the glycoloxide failed when carried out in DMF and nitrobenzene. Such a condensation in absence of any solvent gave a thick liquid, highly soluble in common organic solvents

CCC 0021-8995/88/030561-06$04.00

TABLE I
Characteristics of Polyethers

Polyether	Color	Yield	n (%)		$\overline{M}_n \pm 100$ by VPO	$[\eta]$ ($dL\,g^{-1}$)	TGA data		
			Found	Expected			$IDT \pm 5K$	$IPDT \pm 10K$	E_a ($kJ\,mol^{-1}$)
DCQ-EG	Yellow	73	7.2	7.5	8800	0.14	636	896	67
DCQ-PG	Yellow	69	6.8	7.0	8500	0.12	587	838	84
DCQ-BD	Gray	64	6.1	6.5	8500	0.12	599	844	88
DCQ-DEG	Brown	72	5.8	6.1	7900	0.10	546	813	73
DCQ-TEG	Brown	70	4.8	5.1	8300	0.09	546	816	67
6-MeO-DCQ-EG	Yellow	76	6.2	6.5	8700	0.14	605	899	67
6-MeO-DCQ-PG	Yellow	65	5.9	6.1	8200	0.13	590	851	88
6-MeO-DCQ-BD	Yellow	65	5.4	5.7	8300	0.13	555	845	84
6-MeO-DCQ-DEG	Gray	72	5.0	5.4	8000	0.1	560	815	80
6-MeO-DCQ-TEG	Brown	71	4.3	4.6	8500	0.09	580	825	67
6-Me-DCQ-EG	Yellow	69	6.7	7.0	8600	0.15	599	898	67
6-Me-DCQ-PG	Yellow	68	6.3	6.5	8200	0.11	590	845	84
6-Me-DCQ-BD	Gray	60	5.7	6.0	8200	0.12	578	850	88
6-Me-DCQ-DEG	Brown	75	5.3	5.7	7900	0.1	550	825	80
6-Me-DCQ-TEG	Brown	65	4.4	4.8	7800	0.08	562	829	71

like ethanol. The only condition under which the reaction between a DCQ and a glycol could be effected comprised use of polyphosphoric acid as a reaction medium. The typical polymer synthesis is described here.

Condensation of DCQ with Ethylene Glycol (EG) in Polyphosphoric Acid

A carefully prepared solution of DCQ (2.0 g, 0.01 mol) and well dried ethylene glycol (1.1 g, 0.01 mol) in polyphosphoric acid (20 g) was heated at 215–220°C for 6 h. The cooled reaction mixture in the form of a turbid thick liquid was mixed with water (250 mL) with very rapid stirring. The mixture was neutralized with aqueous alkali. The solid was filtered and washed with water. The dried solid was then treated thrice with boiling benzene (2.0 mL), and then washed with hot acetone (20 mL). A yellow colored powder was obtained. The polyether sample is designated as DCQ-EG. Its yield was 73%. It is soluble in DMF and formic acid.

ANAL. Calcd. for: $C_{11}H_9NO$ (171.4): N 7.5%. Found: N 7.1%.

Other polyethers prepared in the same manner are described in Table I.

The characteristics of the polyethers were measured following usual methods employed for the purpose. For the measurement of electrical conductivity, a 100 mesh size powder was pressed into a cylindrical pellet at a pressure of 10^4 psi. The diameter of the pellet was 1.0–1.1 cm and the thickness was 3–5 mm. The actual dimensions of each pellet were measured. Each side of the pellet was covered with a thin silver paste. The pellet was placed between two electrodes of Hewlett Packard 4329 A High Resistance Meter for measuring its resistance. Measurements were carried out at various temperatures up to 150°C. The values of specific conductance (σ) estimated from observed values of resistance and the size of the pellet.

Polymer Characteristics

The polyethers were yellow to brown colored solids. The yields of the polyethers and their characteristics are described in Table I. They were formed in yields ranging from 60 to 70%. They were insoluble in organic solvents including tetrahydrofuran (THF) and dimethylsulfoxide (DMSO). They did not fuse when heated up to 300°C. These polyethers can be considered to be poly(heteroarylene alkylene ether)s. It was not surprising that they shared the properties of polyphenylene-methylene ethers. The latter are reported to be infusible and insoluble in common solvents.

Examination of the values of the number average molecular weight of the polyether samples revealed that they ranged from 7700 to 8700 depending upon the nature of the monomers employed for the polyether synthesis. Among the polyethers prepared from the same dichloroquinoline with different aliphatic diethers, the order of number average molecular weight was
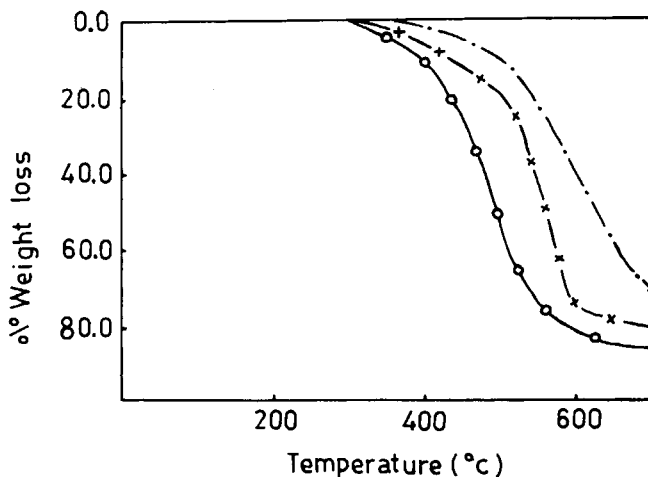
DCQ-PG > DEQ-BD > DEQ-EG > DCQ-TEG > DCQ-DEG

Fig. 1.   (●) DCQ-EG; (×) DCQ-BD; (○) DCQ-PG.

The intrinsic viscosity of polymer sample measured in DMF, varied from 0.07 dL g^{-1} to 0.15 dL g^{-1}; the value estimated by the application of both the Huggins,[11] and Kraemer[12] relations agree very well. Infrared (IR) spectra of all the polyether samples comprise characteristics of 2,4-disubstituted or 2,4-trisubstituted quinoline as the case may be. The spectra exhibit expected bands at 3060 cm^{-1}, in the region from 1700 to 1450 cm^{-1} and in the region from 900 cm^{-1} to 770 cm^{-1}. The presence of end—CH$_2$OH group in the polymer sample is reflected in its IR spectrum which comprises a broad band characteristic of O—H stretching extending from 3600 cm^{-1} to 3300 cm^{-1} with a maximum around 3430 cm^{-1}. The spectra comprise a band at 1360 cm^{-1} which can be assigned to —OH deformation,[13] bands at 1230 cm^{-1} and 1150 cm^{-1}, which can be assigned to C—O—C stretching[14] and a band at 1010 which may be due to C—O stretching of alcohols.[15]

The thermal gravimetric analysis (TGA) data were analyzed by the method of Doyle[16] to estimate initial decomposition temperature (IDT) and integral procedure decomposition temperature (IPDT) and by the Broido[17] method and also by the Anderson and Freeman[18] method to estimate kinetic parameters of the thermal degradation reaction. The values of these parameters are presented in Table I; selected thermograms and Broido plots are presented in Figures 1 and 2, respectively. The Broido plot for the degradation of each polyether sample is found to be linear, indicating that the degradation of each polyether sample is a one-step reaction. Considering the values of either IDT or IPDT as a measure of relative thermal stability it can be inferred that among the polyethers prepared from the same DCQ monomer, the polyether prepared from EG is the most stable, next in the order of stability are the polyethers prepared from PG and BD and the last in the order are the polyethers prepared from DEG and TEG. The energy of activation of degradation of polyethers range from 70 to 90 kJ mol^{-1}. The value of energy of activation estimated by the application of the Anderson and Freeman[18] also turns out to be the same as that estimated on the basis of Broido method.[17] Analysis of the TG data by Anderson and Freeman method[18] has revealed
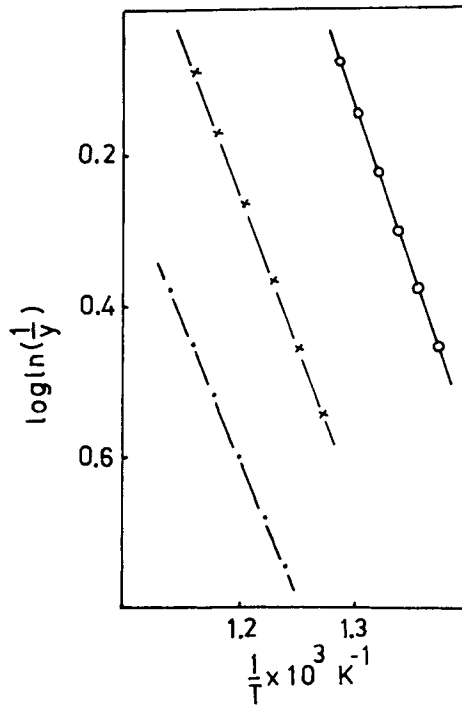
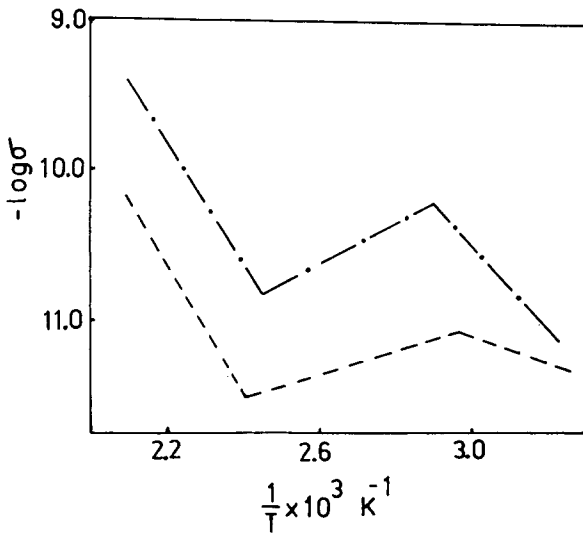Fig. 2.   (●) DCQ-EG; (×) DCQ-BD; (○) DCQ-PG.

Fig. 3.   (●) DCQ-PG; (---) DCQ-EG.

that degradation reaction of each polyether is first order as the estimated value of the order of each degradation reaction is found to be around 1. This supported the assumption made while applying Broido's method[17] that the thermal degradation reaction for polyether is a first-order reaction.

The specific conductance of the polyether sample at around 30°C is found to range from 10^{-11} to 10^{-12} Ohm^{-1} cm^{-1} and is found to increase to 10 to 50 times its value at 30°C for ~ 100° rise in temperature. In order to examine the manner in which σ changes with temperature, plots of log σ versus $1/T$ were made.[19] The selected plots are shown in Figure 3. It is seen that the variation in σ with temperature in terms of an Arrhenius type relation[19] is not linear throughout the range of study.

The work presented here reveals that a 2,4-dichloroquinoline can function as a monomer for synthesis of polyether of sufficiently high thermal stability. The molecular weight of the polyether formed does not rise above ~ 9000, indicating lower reactivity of this monomer. The present study revealed that these materials can be ranked as insulators.

References

1. L. Valentine and R. W. Winter, *J. Chem. Soc.*, 4768 (1956).
2. M. Sittig, *Polyacetal Resins*, Gulf Publishing, Houston, 1963.
3. W. H. Linton and H. H. Goodman, *J. Appl. Polym. Sci.*, 1(2), 179 (1959).
4. W. H. Linton, *Trans. Plastics Inst.*, 28 (75), 131 (June 1960).
5. G. F. Endres and J. Kwiatek, *J. Polym. Sci.*, 58, 593 (1962).
6. R. D. Deanin and A. V. Pinter, U.S. Pat. 3,203,926, (Cl. 260-47), Aug. 31, 1965; *Chem. Abstr.*, 64, 3778e (1966).
7. M. L. Belli, G. Illuminati, and G. Marino, *Tetrahedron*, 19 345 (1963).
8. F. D. Chattaway and J. M. D. Olmsted, *J. Chem. Soc.*, 97, 938 (1910).
9. C. M. Mehta and G. H. Patel, *J. Sci. Ind. Res.*, 18B, 391 (1959).
10. G. Koller, Ber. 60B 1108–11 (1927); *Chem. Abstr.*, 21, 2475^2 (1927).
11. M. L. Huggins, *J. Am. Chem. Soc.*, 64, 2716 (1972).
12. E. O. Kraemer, *Ind. Eng. Chem.*, 30, 1200 (1938).
13. Lecomte, *Compt. Rend. Acad. Sci. Paris*, 180, 825 (1925).
14. L. J. Bellamy, *The Infra-red Spectra of Complex Molecules*. Chapman and Hall Ltd., London, 1975.
15. H. Zeiss and M. Tsutsui, *J. Am. Chem. Soc.*, 75, 897 (1953).
16. C. D. Doyle, *Anal. Chem.*, 33(1), 77 (1961).
17. A. Broido, *J. Polym. Sci.* A-2, 7, 1761 (1969).
18. D. A. Anderson and E. S. Freeman, *J. Polym. Sci.*, 54, 253 (1961).
19. J. Danhaeuser and G. Manecke, *Makromol. Chem.*, 84, 238–249 (1965).