Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article Patel, Pradip S. and Patel, Shanti R.(1987) 'Friedel-Crafts Polymers. 9. Friedel-Crafts Polycondensation of 4,4'-Dichloroacetyldiphenyl Ether with Phenols', Journal of Macromolecular Science, Part A, 24: 1, 67 — 74
To link to this Article: DOI: 10.1080/00222338708058509
URL: http://dx.doi.org/10.1080/00222338708058509

J. MACROMOL. SCI.—CHEM., A24(1), pp. 67-74 (1987)

FRIEDEL-CRAFTS POLYMERS. 9. FRIEDEL-CRAFTS POLYCONDENSATION OF 4,4′-DICHLOROACETYLDIPHENYL ETHER WITH PHENOLS

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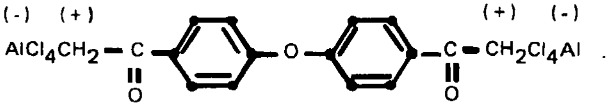
ABSTRACT

The Friedel-Crafts polycondensation of 4,4′-dichloroacetyldiphenyl ether (DADE) with phenol, *o*- and *p*-chlorophenols, and isomeric cresols was carried out in the presence of different molar proportions of $AlCl_3$ under different experimental conditions, proving that this dichloro monomer is a much weaker reagent than dichloromethyldiphenyl ether and *p*-xylylene dichloride in Friedel-Crafts polycondensation. The polyketoethers thus prepared from DADE under identical conditions are characterized by elemental analysis, IR spectral study, viscometric measurements in dioxane, and estimation of $\bar{M}_n$ by nonaqueous conductometric titration and by TGA in air. The polyketoethers are reduced by the Wolf-Krishner reaction. The properties of the reduced polyketoethers, which show no C=O bands in their IR spectra, are compared with those of their corresponding parent polyketoethers.

INTRODUCTION

There are reports about the formation and characterization of Friedel-Crafts polymers formed by self-polycondensation of *p*-xylylene dichloride (PXDC) [1], *p,p*′-dichloromethyldiphenyl ether (DDE) [2], and by Friedel-Crafts polycondensation of each of these with benzene [3-5], toluene [4-6], isomeric xylenes [7-10], and isomeric chlorotoluene [4, 10, 11]. It is reported that polymers formed by using higher proportions of anhydrous aluminum chloride and under comparatively milder conditions are insoluble in common organic solvents [4, 7, 8, 10], due to the sparse crosslinking between active sites on the polymer chains by intermolecular Friedel-Crafts reaction through the dichloride monomer [2, 4, 10]. The active sites for the intermolecular Friedel-Crafts reaction are present on the $-CH_2-Ph-CH_2-$ or $-CH_2-Ph-O-Ph-CH_2-$ repeat units of the polymer chains [2, 4, 10]. Both PXDC and DDE have proven to be very active in Friedel-Crafts polycondensation due to the ease of formation of the corresponding Friedel-Crafts complex, $\mathrm{Al}\overset{(-)}{\mathrm{Cl}}_4-\overset{(+)}{\mathrm{C}}\mathrm{H}_2-\mathrm{Ar}-\overset{(+)}{\mathrm{C}}\mathrm{H}_2-\overset{(-)}{\mathrm{Cl}}_4\mathrm{Al}$. The Friedel-Crafts polycondensation of dichloride monomers, like PXDC and DDE, with active aromatic compounds occurs under comparatively milder reaction conditions. In contrast, such a reaction of 4,4′-dichloroacetyldiphenyl ether (DADE) with active aromatic compounds may not be facile due to the presence of the C=O group attached to the diphenyl ether moiety of DADE molecule. The presence of the C=O group should yield the Friedel-Crafts complex,



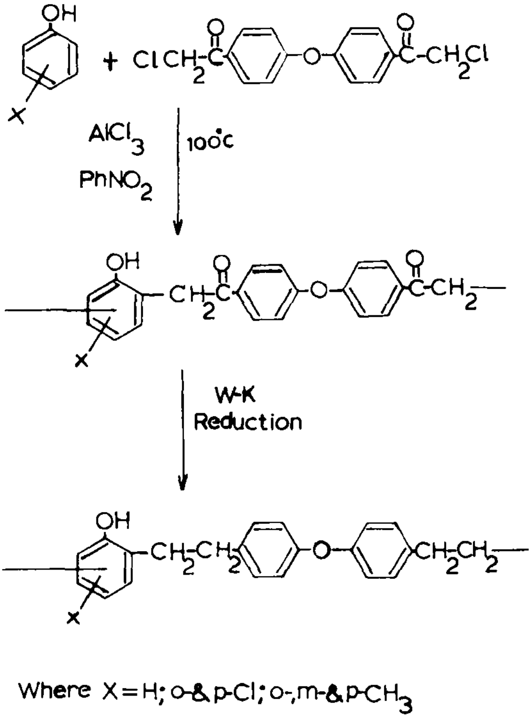
much less stable and make formation of the complex more difficult and, thereby, render DADE less reactive in the present type of reaction. This has also been reported in one of our recent publications in this series [11].

It is further substantiated by the present work which deals with the Friedel-Crafts polycondensation of DADE with equimolar amounts of phenol, isomeric cresols, and *o*- and *p*-chlorophenols (Scheme 1).

EXPERIMENTAL

Materials

The monomer 4,4′-dichloroacetyldiphenyl ether (DADE) was prepared by the literature method [13]. Anhydrous aluminum chloride, hydrazine hydrate, nitrobenzene, phenol, *o*- and *p*-chlorophenols, and isomeric cresols were laboratory grade reagents. The phenols were purified by distillation.



SCHEME 1.

FRIEDEL-CRAFTS POLYCONDENSATION

The amount of anhydrous aluminum chloride ($AlCl_3$) used in the reaction was either 1 or 3 moles per mole of the monomer. The reactions were attempted in the absence of any solvent at room temperature and in the presence of solvents like CS_2 and dioxane at reflux temperature and in the presence of nitrobenzene either at 100 or 200°C.

The polymer samples formed on condensation of a phenol with DADE in the presence of $AlCl_3$ in a molar ratio of 1:1:3 and in nitrobenzene at 100°C for 2 h were characterized. These polymer samples were reduced by the Wolf-Krishner method of reduction [12]. The resulting products were characterized and compared with their parent polymers with a view to studying the effect of reduction of carbonyl group in the repeat units of the polymer chains to methylene group.

Well-powdered anhydrous aluminum chloride (4.0 g, 0.03 mol) was added in small lots with stirring to a mixture of DADE (3.22 g, 0.01 mol) and phenol (0.94 g, 0.01 mol) in nitrobenzene (5 mL). The reaction mixture was heated at 100°C for 2 h. The cooled mixture was poured into a 1:1 water:HCl mixture (100 mL) with stirring. It was filtered and treated with boiling 5% HCl solution (50 mL). The dark brown colored solid thus obtained was steamed to remove adhering nitrobenzene. It was then filtered and dried in air. The solid was refluxed with petroleum ether (60-80°C) for 30 min. The polymer sample was designated as DADE-PhI. The yield was 2.9 g. It was insoluble in all common solvents and did not melt up to 360°C.

Polycondensation of DADE with chlorophenols and cresols were effected in a similar manner. They are designated as indicated in Table 1.

Wolff-Kishner Reduction

A mixture of DADE-PhI (3.45 g, 0.01 mol), diethylene glycol (20 mL), hydrazine hydrate (99.0%) (5.0 mL), and potassium hydroxide pellets (4.0 g) was warmed on a boiling water-bath until the KOH dissolved. The reaction mixture was then heated under reflux for 10 h. The resultant reaction mixture was diluted with water (20 mL) and just neutralized by dilute HCl. The reduced polymer sample was filtered, washed with water, and dried. The yield was 3.2 g. It was insoluble in all common organic solvents and did not melt up to 360°C. This sample was designated as DADE-PhIA.

Apparatus and Methods of Characterization

Elemental analyses of the polymer samples listed in Table 1 were carried out on a Coleman Analyzer. The chlorine estimation was done by the Carius method. IR spectra of the polymer samples were taken in KBr on a UR-10 IR spectrophotometer. Conductometric titration of all the polymer samples with standard sodium methoxide in pyridine was carried out with a Metrohm Herisan Konductoskop E 365 according to the details described by Chatterjee [14]. The viscosities of solutions of soluble polymer samples were measured in dioxane at 35 ± 0.1°C in a Ubbelohde-type dilution viscometer. Thermogravimetric analysis of all the polymer samples was carried out on a Linseis (Germany) thermogravimetric analyzer in air at a heating rate of 10°C/min. The results are in Table 2.

TABLE 1. Characterization of the Polyketoethers

				Elemental analysis				Huggins relation		Kraemer relation	
No.	Polymer sample	Yield, %	Melting range, °C	C, %	H, %	Cl, %	$\bar{M}_n$ [b] ± 100	$[\eta] \times 10^3$, [c] dL/g	*K*	$[\eta] \times 10^3$, [c] dL/g	*K*
I	DADE-Phenol	90.0	>360	75.50	4.50	1.1	3 500	-	-	-	-
IA	W-K of I[a]		>360	83.30	5.40	-	3 400	-	-	-	-
II	DADE-*o*-chlorophenol	50.0	75-90	68.60	3.90	10.6	3 000	89.5	0.269	89.3	0.237
IIA	W-K of II[a]		78-98	74.60	4.85	-	3 000	89.0	0.260	89.0	0.237
III	DADE-*p*-chlorophenol	56.0	125-140	68.60	3.90	10.4	3 100	101.0	0.327	101.3	0.201
IIIA	W-K of III[a]		130-142	75.00	4.85	-	2 900	101.0	-	-	-
IV	DADE-*o*-cresol	63.0	>360	75.30	5.10	0.98	3 600	95.0	0.293	94.6	0.193
IVA	W-K of IV[a]		>360	84.20	6.08	-	3 500	94.3	0.267	94.0	0.233
V	DADE-*m*-cresol	72.0	>360	76.20	5.20	0.88	4 000	-	-	-	-
VA	W-K of V[a]		>360	84.10	6.10	-	3 800	109.8	0.383	106.1	0.123
VI	DADE-*p*-cresol	73.0	Softens at 170-190	74.80	5.2	0.93	3 800	105.0	0.352	104.3	0.230
VIA	W-K of VI[a]		175-190	84.10	6.10	-	3 600	105.0	0.303	105.2	0.179

[a] Wolff-Kishner reduction product formed in nearly quantitative yield.

[b] By nonaqueous conductometric titration.

[c] In dioxane.

TABLE 2. Thermogravimetric Analysis in Air at a Heating Rate of 10°C/min

Polymer sample no.	% weight loss at a temperature of (°C) 250	300	400	500	600	Energy of activation, $E \pm 5\%$, kcal/mol
I	3.5	6.5	25.5	55.0	92.0	46.6
IA	2.8	5.0	23.0	50.3	90.0	42.0
II	3.0	13.5	28.0	43.5	89.0	38.0
IIA	2.5	11.7	22.0	40.2	79.5	35.0
III	6.0	12.0	20.0	36.0	73.0	37.0
IIIA	5.6	12.0	20.0	30.0	70.0	36.0
IV	8.0	15.3	28.0	40.6	89.0	32.6
IVA	8.7	14.2	26.6	32.8	84.0	32.0
V	5.0	12.0	28.5	39.5	68.5	30.0
VA	32.0	10.0	24.7	40.0	65.3	28.0
VI	2.9	20.0	26.5	49.3	87.6	35.0
VIA	3.0	18.5	24.2	48.3	83.9	34.0

RESULTS AND DISCUSSION

The systematic study of the Friedel-Crafts polycondensation of DADE with the six phenols listed in Table 1 reveals that DADE is a much weaker reagent than DDE and PXDC. When milder reaction conditions were employed, the reaction failed or gave a very poor yeild. Such products dissolve partly in acetone and MEK and completely in DMF, and they fuse over a temperature range between 110 and 150°C.

The Friedel-Crafts polycondensation polymers which were characterized are formed under similar experimental conditions at 100°C by using the two monomers and aluminum chloride in a 1:1:3 mole ratio. These polymer (Table 1), which can also be termed polyketoethers, are insoluble in common solvents like acetone, MEK, and ethanol. They are soluble in dioxane except for the sample prepared from phenol. The polyketoethers prepared from phenol as well as *o*- and *m*-cresols do not fuse up to 360°C. The lower yields of polymers formed from *o*- and *p*-chlorophenols indicate lower reactivity of chlorophenol. The polymer products formed under the same conditions but at higher temperatures were insoluble in all solvents, and yields were 60 to 85%, depending upon the nature of the phenol monomer.

The values of $\bar{M}_n$ estimated by conductometric titration [14] agree fairly well with those estimated by endgroup analysis. This suggests that every polymer chain ends on one side in a $-CH_2Cl$ group. The $\bar{M}_n$ of each reduction product agrees reasonably well with the value expected from $\bar{M}_n$ of the parent polyketoether.

The reduced viscosity in the dioxane solution of all the polymer samples is around 0.1 dL/g. The intrinsic viscosity estimated by the application of the Huggins [15] and the Kraemer relations [16] are nearly equal. As expected, the sum of the Huggins and the Kraemer constants is around 0.5 dL/g [17].

The IR spectra of these polymer samples show a carbonyl band at 1 680 cm^{-1}. The carbonyl band in the spectrum of monomer DADE appears at 1 710 cm^{-1} ;11]. The polymer samples also show bands at 880 and 815 cm^{-1}, characteristic of isolated and two adjacent H atoms, respectively. The band characteristic of a biphenyl ether system is observed at 1 250 cm^{-1}. In the reduction products the band at 1 680 cm^{-1} is absent, indicating that almost all the carbonyl groups have been reduced.

There is no conspicuous change in the melting behavior and solubility of the polyketoethers on reduction.

The results of IGA show that all the polymer samples lose 3-8 wt% when heated to 250°C and around 40-50 wt% when heated to 500°C. Analysis of the TGA data by the Broido method [18] reveals that the energy of activation of the degradation of the polymer samples varies from around 30 to 40 kcal/mol. The effect of the structure of the monomer on the nature of the degradation reaction of polymer is not discernible in the TG data. The reduction products exhibit slightly higher thermal stability up to around 400°C than the corresponding parent polyketoether samples.

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Received September 30, 1985
Revision received January 31, 1986