merization of mixed cyclic diamides appears to be an interesting way of getting to copolyamides of regular structure.

Experimental Section

Monomers. Monomers of high reactivity, for example, *c*-62, were recrystallized until two recrystallizations did not change the infrared spectrum of the compound. (Note: The melting point could not be used as a criterion of purity. *c*-62 starts to polymerize below the melting point and upon dissolution for recrystallization.)

Other cyclic monomers were recrystallized to constant melting point. The purity is believed to be better than 99%. Trace impurities of solvent and moisture were removed by drying the cyclic diamides over P_2O_5 at 0.1 mm and 100° overnight.

Cleaning of Glass Tubes. Glass tubes (4 mm o.d.) were placed into a bath of fuming nitric acid overnight. They were rinsed with distilled water, dried, flamed out, and placed in a 120° oven for several hours. Polymerization tubes of 5 in. length and sealed at one end were made from these glass tubes. *c*-62 is stable for 20 min in the melt at 259°. In nontreated tubes, polymerization starts in 5–10 min.

Polymerization Temperatures. Most polymerizations were carried out in a vapor bath of diphenyl ether (bp 259°). For higher polymerization temperatures, boiling benzophenone (bp 306°) and for lower polymerization temperatures, boiling 1-decanol (bp 234°) were used as the bath liquid. This polymerization temperature gave, however, incomplete melting of *c*-62 because polymerization occurred during the melting process.

Viscosity Measurements. Inherent viscosities of nylon 62 polymer were measured in 0.5% *m*-cresol solutions. The inherent viscosities (η) were between 0.3 and 0.5.

Gas Evolution. Gas evolution during the polymerization of molten *c*-62, *c*-6262, or from solid nylon 62 polymer was evaluated quantitatively as follows (see also ref 23 and 24). The polymerization of *c*-62 or *c*-6262 was carried out in a 2-ml glass tube closed with a serum stopper. Before polymerization the air in the tube was replaced with helium by repeated evacuation and refilling with helium. A 2-cc syringe (no. 17 needle) was inserted into the serum stopper, and the polymerization was carried out at elevated temperatures. The total gas evolution was measured in the syringe. The sample of the gas mixture of CO_2 and CO was analyzed by gas chromatography. Mass spectroscopy of *c*-62 gave as a major fragment CO_2 but not CO.

Solid-State Polymerization of *c*-62. Samples of 0.1 g of *c*-62 without and with 1 mol % of $NaOCH_3$ were placed into tubes and heated under nitrogen to 153° (bromobenzene bath), 196° (ethylene glycol bath), and 222° (methyl salicylate bath). Samples were taken out at different time intervals, and the ir spectrum in Nujol mull was determined. The ratios of the band at 11.8 μ (characteristic for the monomer) to the band at 13.8 μ (characteristic for the polymer) gave the amount of unchanged monomer. A standardization was carried out with known monomer polymer mixtures. No attempt was made to estimate the dimer content.

Polymerization. To a 0.5-ml glass tube were added 50 mg of the cyclic dioxamide and 1 mol % of the initiator in solution ($NaOCH_3$ in CH_3OH). The solvent was removed by evaporation. The polymer tube was repeatedly and alternately flushed with an inert gas and evacuated to remove oxygen. Nitrogen was commonly used as the inert gas, although hydrogen or helium have also been used. The tube was then sealed under one atmosphere of nitrogen and immersed in the condenser of a vapor bath containing refluxing diphenyl ether, bp 259°. The times necessary to form visible polymer using a variety of initiators are listed in Tables I–IV. After the polymerization was complete, the tube was cooled and the polymer removed from the tube. The polymer retains the shape of the cavity of the tube.

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(23) E. P. Krasnov and L. B. Solokov, *Vysokomol. Soedin., Khim. Svoistva i. Modifikatsiya Polimerov Sb. Statei*, 275 (1964).

(24) E. P. Krasnov, L. B. Solokov, and T. A. Polyakova, *Vysokomol. Soedin.*, 6 (7), 1244 (1962).

Syntheses and Investigations of Polymers Containing the 1,2,4-Oxadiazole Nucleus

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ABSTRACT: Polymers containing the 1,2,4-oxadiazole nucleus were synthesized by the 1,3-dipolar cycloaddition of arylenedinitrile oxides to various dinitriles and by the homopolymerization of 3-cyanobenzonitrile oxide. Poly(arylene-1,2,4-oxadiazoles) were also synthesized by cyclodehydration of poly(arylene acyloylamidoximes), prepared by condensation polymerization of arylene diamidoximes and arylene diacid chlorides. Thermogravimetric analyses of polymers prepared by both methods showed thermal degradation below 400°. A number of model compounds were synthesized and their thermal properties were found to be similar to those of the polymers.

Early work by Tiemann and Krüger suggested that 3,5-diphenyl-1,2,4-oxadiazole was exceptionally stable to thermal, oxidative, and hydrolytic degradation.[1] Much later, Blomstrom reported the first synthesis of 1,2,4-oxadiazole polymers by the cyclodehydration of polymeric acyloylamidoximes, but made no mention of the thermal and oxidative stability of these products.[2] The copolymerization of terephthalonitrile di-N-oxide with terephthalonitrile[3] and the homopolymerization of 4-cyanobenzonitrile oxide[4]

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(1) F. Tiemann and P. Krüger, *Chem. Ber.*, 17, 1685 (1884).

(2) D. C. Blomstrom, U. S. Patent 3,044,994 (1962).

(3) C. G. Overberger and S. Fujimoto, *J. Polym. Sci., Part B*, 3, 735 (1965).

(4) M. Akiyama, Y. Iwakura, S. Shiraishi, and Y. Imai, *ibid.*, 4, 305 (1966).

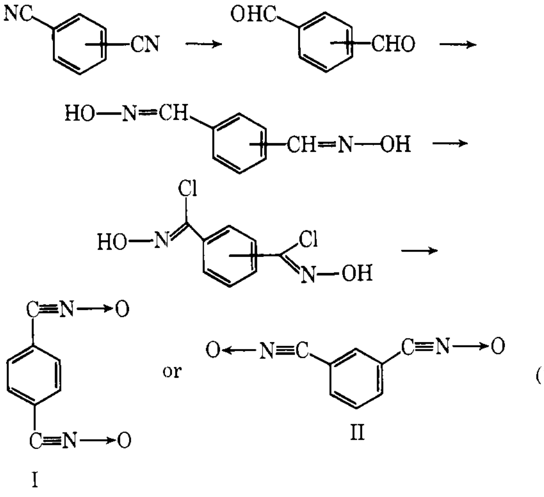
also resulted in the formation of arylene-1,2,4-oxadiazole polymers. Again, the thermal and oxidative stability of these polymers were not reported. It was our objective to synthesize high molecular weight poly(arylene-1,2,4-oxadiazoles) in order to determine whether these polymers would exhibit the necessary thermal and oxidative stability required for high temperature resistant resins.

Since this work was initiated, others have reported the syntheses of low molecular weight poly(arylene-1,2,4-oxadiazoles)[5] and, in three instances,[5a–c] have investigated the thermal stability of these polymers by thermogravimetric analysis (TGA). Furthermore, Cotter and Knight have reported that 3,5-diphenyl-1,2,4-oxadiazole in fact begins to decompose at 340° with cleavage of the oxadiazole ring to give phenyl isocyanate and benzonitrile.[6]

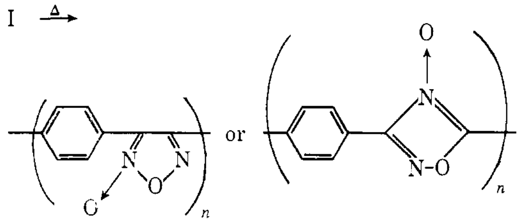
We wish to report the syntheses of polymers containing the 1,2,4-oxadiazole nucleus by 1,3-dipolar cycloaddition reactions and by cyclodehydration of poly(arylene acyloylamidoximes). Even though many of these polymers are much higher molecular weight than those previously investigated, no improvement in thermal stability has been achieved.

Results and Discussion

Polymerization by 1,3-Dipolar Cycloaddition. Terephthalonitrile di-N-oxide (I) and isophthalonitrile di-N-oxide (II) were synthesized by known reaction schemes involving preparation of the corresponding aldehydes[7] and their dioximes, followed by chlorination to the dihydroximic chlorides and subsequent dehydrochlorination[8] (eq 1). Crystalline terephthalonitrile di-N-oxide is stable indefinitely at room temperature. At elevated temperatures it polymerizes to the furoxan or oxazoxime (1,2,4-oxadiazole 4-oxide) (eq 2).[9] Isophthalonitrile di-N-oxide must be prepared and handled at reduced temperature to avoid a similar homopolymerization.

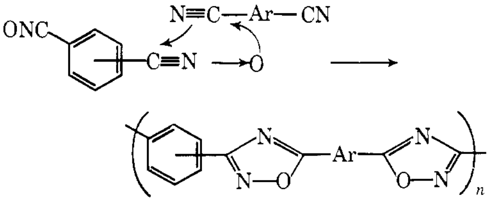


(1)



(2)

To accomplish the desired polymerization it was necessary to design a system which contained a diluent that was inert to the dinitrile oxide and in which the dinitrile oxide was insoluble. In solution, the dinitrile oxide homopolymerizes much more rapidly than it combines with aromatic dinitriles. Polymerizations were carried out by suspending the dinitrile oxide in a solvent for the dinitrile such as diglyme, tetraglyme, veratrole, or tetramethylene sulfone, and stirring rapidly in an inert atmosphere for several days at the desired temperature. Polymerizations using terephthalonitrile di-N-oxide were run at 25°, whereas isophthalonitrile di-N-oxide was used at 0° to prevent furoxan formation (eq 3).



(3)

Copolymerization of these dinitrile oxides with iso- or terephthalonitrile proceeded over 6 days to give near-quantitative yields of snow-white polymers which had inherent viscosities of 0.1 in sulfuric acid, the only solvent found for the polymers. Infrared analyses showed the typical 1,2,4-oxadiazole absorptions at 1560, 915 cm^{-1}, etc., as well as trace absorptions due to nitrile (2220 cm^{-1}) and nitrile oxide (2300 cm^{-1}), probably present as end groups. Stirring for additional lengths of time, or heating the 6-day reaction mixtures in sealed tubes to 250°, caused no increase in the inherent viscosities, although the latter treatment did serve to eliminate the nitrile oxide absorptions in the infrared spectra. The addition of various Lewis acids, a treatment which had been found necessary to cause nitrile oxides to react with alkyl nitriles,[10] did not improve inherent viscosities.

Copolymerizations of the dinitrile oxides with 4,4′-dicyanodiphenyl sulfone proceeded to "completion" in only 3 days, although the inherent viscosity was again 0.1. The faster reaction of this dinitrile was expected because of the electron-withdrawing effect of the sulfone group which renders the nitrile carbon more subject to nucleophilic attack. Copolymerizations with cyanogen and with perfluoroglutaronitrile proceeded extremely rapidly with much heat evolution, necessitat-

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(5) (a) V. V. Korshak, E. S. Krongauz, and A. L. Rusanov *J. Polym. Sci., Part C*, **5**, 2635 (1967); (b) N. Dokoshi, Y Bamba, M. Kurihara, and N. Yoda, *Makromol. Chem.*, **108**, 170 (1967); (c) T. Shono, M. Saga, M. Obora, and K. Shinra, *J. Chem. Soc. Jap., Ind. Chem. Sect.*, **70**, 1250 (1967); (d) Von W. Ratzill and W. Funke, *Makromol. Chem.*, **99**, 1 (1966).

(6) J. L. Cotter and G. J. Knight, *Chem. Commun.*, **11**, 336 (1966).

(7) T. van Es and B. Staskun, *J. Chem. Soc.*, 5775 (1965).

(8) (a) E. J. Frazza, U. S. Patent 3,213,068 (1965); (b) Y. Iwakura, M. Akiyama, and K. Nagakubo, *Bull. Chem. Soc. Jap.*, **37**, 767 (1964); (c) Y. Iwakura, M. Akuyama, and S. Shiraishi, *ibid.*, **38**, 335 (1965).

(9) S. Fujimoto, *J. Polym. Sci., Part B*, **5**, 301 (1967).

(10) S. Morrocchi, A. Ricca, and L. Velo, *Tetrahedron Lett.*, 331 (1967).

ing strong cooling to maintain control of the reaction. The resulting snow-white polymers had the expected 1,2,4-oxadiazole infrared spectra. They were insoluble in all solvents tested including sulfuric acid.

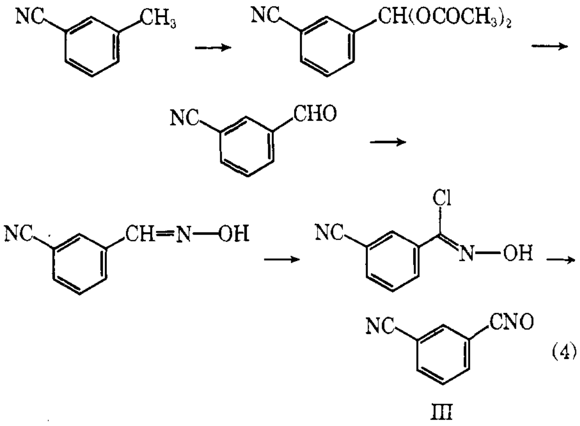
Terephthalonitrile di-N-oxide was also copolymerized with two perfluoroalkyl ether dinitriles. In these

$NC–(CF_2)_4–O–CF(CF_3)–CN$

$NC–CF(CF_3)–O–CF_2CF_2–O–CF(CF_3)–CN$

cases, carbon tetrachloride was used as solvent for both the dinitrile and the resulting polymer. As the mixture was stirred at room temperature the dinitrile oxide slowly dissolved as it polymerized until complete solution was effected after 3 days. After 7 days, polymer was isolated by evaporation of the solvent. The resulting polymers had inherent viscosities of 0.3–0.4 (in CCl_4) and could be compression molded at 100° to form relatively stiff, tough, colorless and transparent films. When these polymerizations were conducted in diglyme, in which the polymer is insoluble, only low molecular weights could be attained. Apparently, the low molecular weight is a consequence of precipitation of the polymer before it can grow to high molecular weight form.

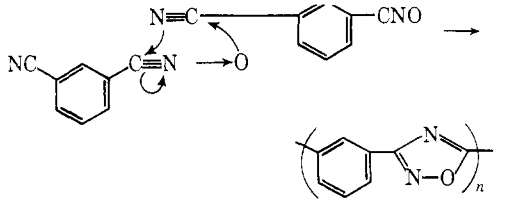
Another approach to polymerization by 1,3-dipolar cycloaddition involved the synthesis and homopolymerization of 3-cyanobenzonitrile oxide (III). Synthesis of this compound from *m*-tolunitrile was accomplished using methods similar to those used for the dinitrile oxides (eq 4). The final step, dehydrochlorination,



(4)

III

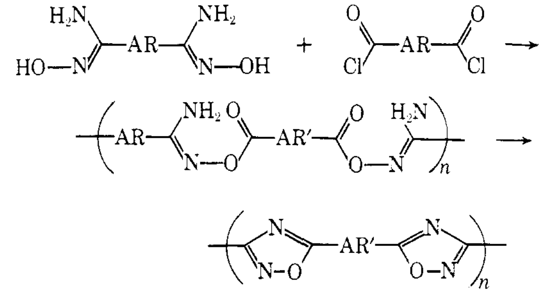
was carried out at −80° and the resulting precipitated monomer was isolated and allowed to warm to room temperature slowly to avoid explosive reaction. Polymerization in the crystalline state could be followed by disappearance of the nitrile oxide (2300 cm^{-1}) and nitrile (2220 cm^{-1}) infrared absorptions and formation of new bands at 1560 and 915 cm^{-1} due to 1,2,4-oxadiazole. After 14 days no further change was noted and the resulting slightly yellow polymer had an inherent viscosity of 0.18 in sulfuric acid. Heating this powder at 250° for 2 hr removed the trace amount of residual nitrile oxide and caused formation of light tan polymer having an inherent viscosity of 0.21. Presumably, as postulated for the solid-state polymerization of 4-cyanobenzonitrile oxide,[4] the crystal structure is such that each nitrile group is associated with a nitrile oxide and a simple rearrangement of bonds gives rise to polymeric oxadiazoles (eq 5).



(5)

Thermogravimetric analyses of the polymers formed by reaction of I or II with arylene dinitriles (Figure 1, curve A) all showed *ca.* 50% weight loss at 325–375°, whether in nitrogen or air, and an additional 50% weight loss at 500–600° in air. The observation that the polymers show identical behavior in nitrogen or air up to 500° is in agreement with their reported chemical inertness to strong oxidizing agents. Surprisingly, poly(1,3-phenylene-1,2,4-oxadiazole) (Figure 1, curve B), prepared by solid-state polymerization of 3-cyanobenzonitrile oxide, exhibited somewhat greater thermal stability, undergoing *ca.* 50% weight loss at 375–425° in nitrogen or air.

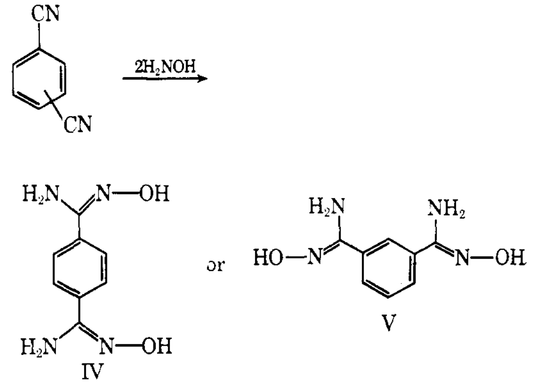
Polycondensation and Cyclodehydration. Blomstrom[2] and, more recently, several other groups[5] have reported the syntheses of poly(arylene acyloylamidoximes) and their subsequent cyclodehydration to poly(arylene-1,2,4-oxadiazoles) (eq 6). We have employed



(6)

this general synthetic route to achieve higher molecular weight products than previously reported, and to study the effect of different arylene nuclei on attainable molecular weight, ease of cyclodehydration and polymer thermal stability.

Terephthalamide dioxime (IV) and isophthalamide dioxime (V) were synthesized from the corresponding dinitriles by reaction with neutralized hydroxylamine hydrochloride in aqueous ethanol (eq 7). Rigorous



(7)

IV

V

purification of the monomers was found to be necessary in order to achieve high molecular weight poly(arylene acyloylamidoximes). These diamidoximes were polymerized with tere- and isophthaloyl chlorides

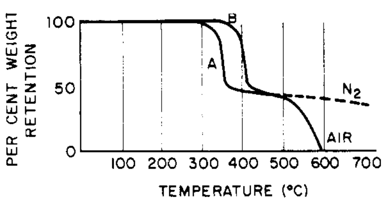


Figure 1. Thermogravimetric analyses of poly(arylene-1,2,4-oxadiazoles): A, copolymers of dinitrile oxides and iso- or terephthalonitrile or 4,4′-dicyanodiphenyl sulfone; B, homopolymer from 3-cyanobenzonitrile oxide.

and 4,4′-bibenzoyl chloride (Table I). Various amide solvents such as dimethylacetamide (DMAc), N-methylpyrrolidone (NMP) or hexamethylphosphoramide (HMPA) could be used, although DMAc gave the best results. The presence of a slight excess of an HCl acceptor was found to be necessary for the formation of high molecular weight polymer. N,N-Diethylcyclohexylamine was preferred, although triethylamine, pyridine and N,N-diethylaniline could also be used. No solvent system was found for polymers VI and VII in which all arylene units are *para* substituted, as is also true of all-*para*-substituted polyamides[11] and polyhydrazides.[5a,12] Polymers IX and X, derived from *p*-diacid chlorides, were soluble in the amide solvents only when 1–10% lithium chloride was added. Polymers VIII and XI, derived from *m*-diacid chloride, were completely soluble in the absence of lithium chloride. Thin films, which were colorless, transparent, strong and flexible, could be cast from DMAc, containing lithium chloride where necessary.

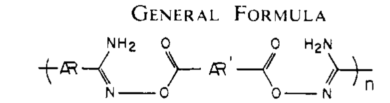
Cyclodehydration to the desired 1,2,4-oxadiazole polymer was accomplished by two methods. The cast films were heated under reduced pressure for 2–3 days at 202 or 218° followed by 2–3 hr at 259°. Heating at lower temperatures caused extremely slow reaction with no improvement in the final product. Heating at higher temperatures gave blistered films which were lower molecular weight. Films obtained from the best thermal cyclodehydrations were light tan to dark brown, transparent and brittle. Infrared analysis confirmed the formation of the desired structure by the disappearance of bands at 3400 cm^{-1} (–NH$_2$) and 1740 cm^{-1} (carbonyl) and the formation of new bands at 1560 and 915 cm^{-1} due to 1,2,4-oxadiazole.

Cyclodehydration was also accomplished by heating solutions of the polymers in amide solvents or dimethyl sulfoxide, containing lithium chloride for polymers IX and X, at 115–120° for 3 days and then at 150° for 2 hr. The 1,2,4-oxadiazole polymers gradually precipitated as white to dark brown solids depending on the solvent employed (DMSO < DMAC < NMP ≅ HMPA). Traces of added tertiary amines caused an increase in the reaction rate and allowed slightly lower temperatures to be used. The presence of acids or acid anhydrides inhibited the cyclodehydration and in several cases caused extensive hydrolysis.

The highest inherent viscosities were obtained by cyclodehydration of poly(arylene acyloylamidoximes) derived from the two *p*-diacid chlorides, terephthaloyl chloride and 4,4′-bibenzoyl chloride (with isophthalamide dioxime as comonomer). That this was not due to the presence of lithium chloride was shown by the solution cyclodehydration of polymer VIII in DMAc containing lithium chloride and by casting a film of polymer VIII from DMAc containing lithium chloride and subjecting it to the identical cyclodehydration conditions used for polymers IX and X. No improvements in inherent viscosities were obtained (Table II).

Table I

Poly(arylene acyloylamidoximes) of General Formula



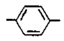
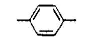
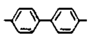
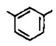
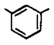
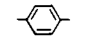
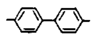
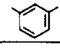
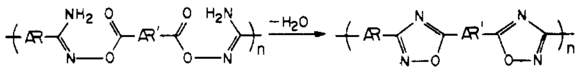
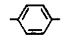
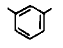
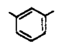
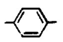
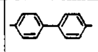
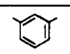
NUMBER	Ar	Ar′	INHERENT VISCOSITY 0.2% in DMAc (30°)
VI			INSOLUBLE
VII	"		INSOLUBLE
VIII	"		1.17
IX			0.99 (+LiCl)
X	"		1.51–2.64(+LiCl)
XI	"		0.81

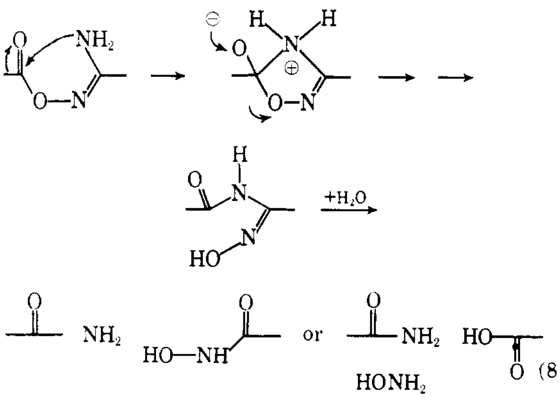
Table II

Cyclodehydration of Poly(arylene acylamidoximes) to Poly(arylene-1,2,4-oxadiazoles)



NUMBER	Ar	Ar′	INHERENT VISCOSITY 0.2% in H_2SO_4(30°)	
			FILM	SOLUTION
VIII → VIII′			0.31	0.27
IX → IX′			0.36	0.44
X → X′	"		0.46	0.47
XI → XI′	"		0.33	0.30

Infrared spectra of the films obtained from thermal cyclodehydrations of cast films exhibited a weak absorption at 1680 cm^{-1} (amide or hydroxamic acid) and, occasionally, weak bands at 1710 cm^{-1} (carboxylic acid) and 2220 cm^{-1} (nitrile). Amide and acid formation could conceivably arise during cyclodehydration



(8)

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(11) (a) J. Preston, *J. Polym. Sci., Part A*, 4, 529 (1966); (b) S. Nishizaki and A. Fukami, *ibid.*, 4, 2337 (1966).

(12) A. H. Frazer, W. Sweeny, and F. T. Wallenberger, *ibid.*, 2, 1157 (1964).

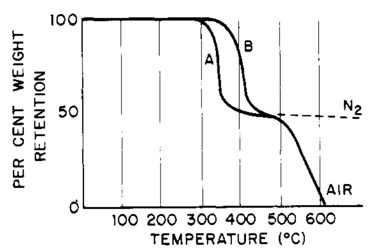
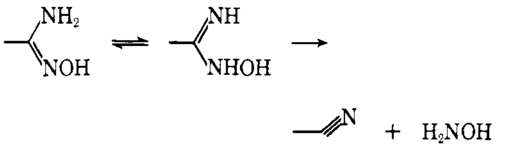
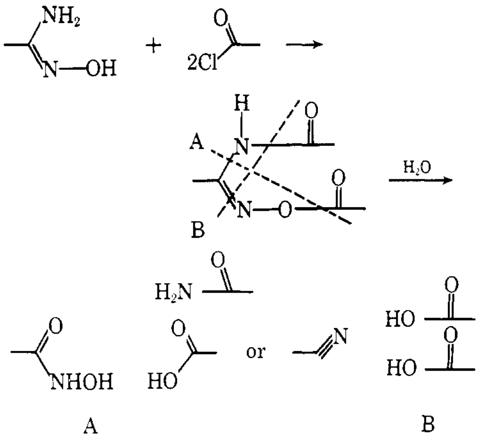


Figure 2. Thermogravimetric analyses of poly(arylene-1,2,4-oxadiazoles): A, polymers VIII′, IX′, XI′; B, polymer X′.

by attack of $-NH_2$ on carbonyl followed by rearrangement and hydrolysis (eq 8). Formation of nitrile could be explained by loss of the elements of hydroxylamine from end-group amidoxime units (eq 9).


(9)

Alternatively, amide formation could occur in the original polymerization by reaction of acid chloride with $-NH_2$. This would not be detected by infrared analysis because of the strong carbonyl absorption at 1740 cm^{-1} and $-C{=}N-$ absorption at 1640 cm^{-1}. Thus, chain branching would occur in the poly(arylene acyloylamidoxime), preventing subsequent cyclodehydration at the branch points. Rather, at these high temperatures the branch points would be hydrolyzed by product water to give the various functional groups detected by infrared analysis. This type of chain cleavage might well be a contributing factor to the lower inherent viscosities of the cyclodehydrated films (eq 10).

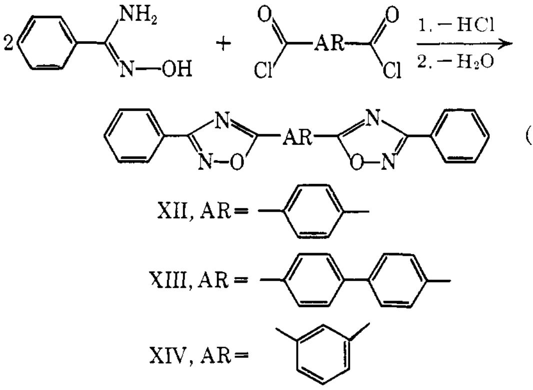

(10)

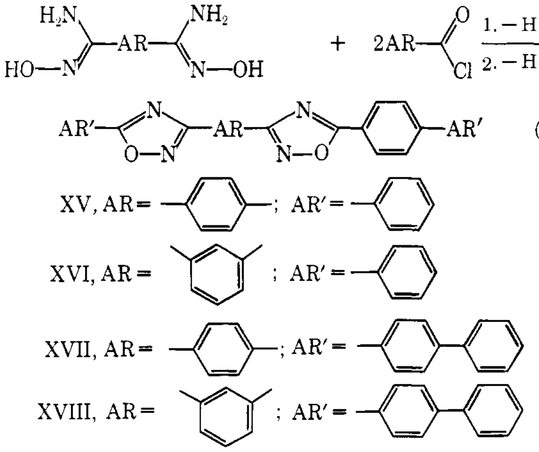
To test this proposal, terephthalamide dioxime was condensed with a 10 mol % excess of isophthaloyl chloride. A film was cast from DMAc and the thermal cyclodehydration was carried out by the normal procedure. Infrared analysis of the resulting film showed a much more intense absorption at 1680 cm^{-1}, suggesting that branching and subsequent hydrolysis at the branch points had indeed occurred.

Attempts to prevent this small amount of amide formation by using a 1–2 mol % excess of diamidoxime in the original polymerizations caused only very small improvements in the cyclodehydrated products and did not completely eliminate the 1680-cm^{-1} absorption. The use of a greater excess of diamidoxime caused a large reduction in the molecular weight of the poly(arylene acyloylamidoxime).

Thermogravimetric analyses of the poly(arylene-1,2,4-oxadiazoles) VIII′, IX′, and XI′, derived from *m*- and *p*-phenylene monomers, indicated *ca.* 50% weight loss at 325–375° in nitrogen or air, followed by an additional 50% weight loss at 500–600° in air (Figure 2, curve A). However, polymer X′, which was synthesized from isophthalamide dioxime and 4,4′-bibenzoyl chloride, exhibited somewhat greater thermal stability undergoing *ca.* 50% weight loss at 375–425° in nitrogen or air (Figure 2, curve B). This increase in thermal stability by incorporating larger arylene nuclei, such as naphthylene or biphenylene, has also been observed in polyamides.[13]

Model Compounds. In the course of this work seven model compounds were prepared by condensation and cyclodehydration (eq 11 and 12). A qualitative com-


(11)


(12)

parison of the relative rates of cyclodehydration indicated that the reaction was favored primarily by *p*-carbonyl units (*viz.* XII faster than XIV) and secondarily by amidoxime units which were not *para* substituted (*viz.* XVI faster than XV). In agreement with these observations is the fact that poly(arylene acyloylamidoximes) IX and X, derived from *m*-diamidoxime and *p*-diacid chlorides, gave the highest molecular weight poly(arylene-1,2,4-oxadiazoles) upon cyclodehydration.

The course of the cyclodehydration reaction appears to involve attack of "electron-rich" nitrogen (best attained by *meta* substitution) on "electron-poor" car-

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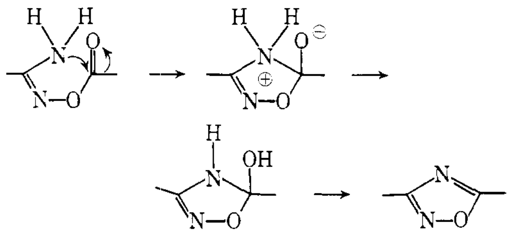
(13) (a) L. Starr, *J. Polym. Sci. Part A*, 4, 3041 (1966); (b) F. Dobinson and J. Preston, *ibid.*, 4, 2093 (1966).

bonyl (best attained by *para* substitution), followed by loss of the elements of water (eq 13). In support of this proposal is the fact that amines added to the polymer solution facilitate the reaction, presumably by avoiding any protonation of the $-NH_2$ group, whereas added acids prevent cyclodehydration and in some cases cause extensive hydrolysis, indicating protonation of the $-NH_2$ group rather than the carbonyl oxygen.


(13)

Two of the model compounds, XIII and XVIII, were tested for thermal stability by heating samples in sealed tubes at 400° for 3 hr. In both cases the resulting black powder showed infrared absorptions due to aromatic nuclei and carbonyl functions, but no absorption due to 1,2,4-oxadiazole, indicating complete decomposition of the oxadiazole nuclei.

It thus appears that the rather low thermal stability of poly(arylene-1,2,4-oxadiazoles) is due to inherent thermal instability of the 1,2,4-oxadiazole nucleus. Our findings are in general agreement with the results of other workers[5] even though the polymers synthesized and evaluated in this study are of substantially higher molecular weight.

Experimental Section

Terephthalonitrile Di-N-oxide (I). Terephthalaldehyde, mp 114–116°, was prepared in 61% yield from terephthalonitrile by the method of van Es and Staskun.[7] It was converted in 86% yield to the dioxime, mp 220–222°, by treatment with neutralized aqueous hydroxylamine hydrochloride. Complete dichlorination was accomplished by dissolving 10.0 g (0.061 mol) of the dioxime in 250 ml of glacial acetic acid, 50 ml of water, and 150 ml of concentrated hydrochloric acid, and bubbling chlorine gas into the cold stirred solution for 2 hr. The dihydroximic chloride was precipitated by dilution with 1000 ml of water. Recrystallization from chloroform afforded 4.3 g of white crystalline solid, mp 181–183°. Dehydrochlorination was accomplished by dissolving 2.5 g (0.011 mol) of the *p*-benzenedihydroximic chloride in 100 ml of methanol and adding 2.3 g (0.023 mol) of freshly distilled triethylamine over 15 min. After stirring for an additional 15 min, the white solid was separated by filtration, washed with cold methanol, and air dried to give 1.6 g (91%) of white powder, mp 265+°.

Anal. Calcd for $C_8H_4N_2O_2$: C, 60.00; H, 2.50; N, 17.50. Found: C, 59–76; H, 2.75; N, 17.43.

Infrared analysis indicated no homopolymerization to furoxan even after standing at room temperature for 2 weeks.

Isophthalonitrile Di-N-oxide (II). Isophthalaldehyde was prepared[7] in 76% yield, mp 87–89°. The dioxime, mp 190–191°, and dihydroximic chloride, mp 162–163°, were prepared by the above methods. Dehydrochlorination was carried out by dissolving 2.3 g (0.010 mol) of *m*-benzenedihydroximic chloride in 20 ml of methanol in a methanol–ice bath, and then adding 2.0 g (0.020 mol) of freshly distilled triethylamine over 15 min. After stirring for an additional 10 min at −10°, the mixture was filtered and air dried on a cold filter to yield 1.3 g (81%) of white powder. The monomer was used immediately since warming above 0° caused homopolymerization to furoxan homopolymer, sometimes explosively.

Polymerizations of Dinitrile Oxides with Dinitriles. Polymerizations were run by stirring 0.00625 mol of each of the comonomers under a nitrogen atmosphere in 10 ml of diglyme (freshly distilled from lithium aluminum hydride) for the desired time at the desired temperature. The polymers were isolated by filtration and washed with methanol to give quantitative yields of white solids which had the correct infrared spectra. Polymers prepared using arylene dinitriles had inherent viscosities of 0.1 (0.25 g/100 ml of H_2SO_4 at 30°). When cyanogen or perfluoroglutaronitrile was used, the polymerization mixture was prepared by the dropwise addition of a diglyme solution of the dinitrile to a cold slurry of the dinitrile oxide in diglyme. No solvent was found for these polymers.

Polymerizations of Terephthalonitrile Di-N-oxide with Perfluoroalkyl Ether Dinitriles. A mixture of 0.00638 mol of dinitrile, $NC{-}(CF_2)_4\ OCF(CF_3){-}CN$ or $NC{-}CF(CF_3)OCF_2CF_2OCF(CF_3){-}CN$, and 1.020 g (0.00638 mol) of terephthalonitrile di-N-oxide in 7 ml of carbon tetrachloride was stirred for 140 hr at room temperature (solution being complete after *ca.* 50 hr) and then heated to evaporate the solvent. The resulting colorless, glassy polymers had inherent viscosities of 0.3–0.4 (0.25 g/100 ml of CCl_4 at 30°) and could be compression molded at 100° to relatively stiff, tough, colorless, transparent films.

3-Cyanobenzonitrile Oxide (III). 3-Cyanobenzaldehyde, mp 76–78°, was prepared from *m*-tolunitrile *via* chromic acid oxidation.[14] The oxime, mp 135–136°, was prepared from neutralized aqueous hydroxylamine hydrochloride. Chlorination was accomplished by bubbling chlorine into an ice-cold solution of 5.0 g (0.0343 mol) of 3-cyanobenzaldoxime in 125 ml of glacial acetic acid, 50 ml of water, and 50 ml of concentrated hydrochloric acid. The hydroximic chloride was isolated by filtration after diluting with 500 ml of water. Recrystallization from carbon tetrachloride afforded 3.7 g (60%) of white crystalline solid, mp 137–137.5°.

Anal. Calcd for $C_8H_5ClN_2O$: C, 53.19; H, 2.77; N, 15.51; Cl, 19.67. Found: C, 53.25; H, 3.11; N, 15.25; Cl, 19.59.

Dehydrochlorination was carried out by the dropwise addition of 1.2 g (0.012 mol) of freshly distilled triethylamine to a Dry Ice–acetone cooled, serum-capped flask containing 2.0 g (0.0111 mol) of 3-cyanobenzenehydroximic chloride in 20 ml of methanol. After stirring for an additional 40 min, the white solid was collected by filtration on a cold funnel and air dried while allowing to warm to room temperature (slowly to avoid explosive reaction). Polymerization could be followed by infrared analysis and was essentially complete after *ca.* 14 days standing. The resulting slightly yellow polymer had an inherent viscosity of 0.18 (0.25 g/100 ml of H_2SO_4 at 30°).

Terephthalamide Dioxime (IV). A mixture of 100 g (0.78 mol) of terephthalonitrile, 163 g (2.35 mol) of hydroxylamine hydrochloride, and 120 g (1.13 mol) of sodium carbonate in 750 ml of water and 1500 ml of ethanol was refluxed for 18 hr. The reaction mixture was cooled and filtered. The air-dried solid was recrystallized from hot DMAc by adding an equal volume of methanol to give 139 g (91%) of white powder, mp 222–228° dec. Rigorous purification by special techniques afforded 39 g of white powder, mp 229–230° dec.

Anal. Calcd for $C_8H_{10}N_4O_2$: C, 49.48; H, 5.19; N, 28.85. Found: C, 49.20; H, 5.32; N, 28.83.

Isophthalamide Dioxime (V). The synthesis was accomplished in a manner similar to the above procedure. Purification *via* the dihydrochloride and by repeated recrystalli-

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(14) S. M. Tsang, E. H. Wood, and J. R. Johnson, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p 641.

zations from isopropyl alcohol afforded white crystalline solid, mp 200–201°.

Anal. Calcd for $C_8H_{10}N_4O_2$: C, 49.48; H, 5.19; N, 28.85. Found: C, 49.10; H, 5.02; N, 28.83.

Polymerizations of Diamidoximes with Diacid Chlorides. To an ice-cold solution of 0.970 g (0.005 mol) of diamidoxime in 15–60 ml of distilled DMAc under a nitrogen blanket was added 1.628 g (0.0105 mol) of N,N-diethylcyclohexylamine. The diacid chloride (0.005 mol) was then added in portions and the resulting solution was stirred for 2 hr at room temperature. Work-up in two 400-ml portions of water and two 400-ml portions of methanol in a blender, followed by drying in a vacuum oven at 80° for 16 hr, afforded the poly(arylene acyloylamidoxime) in quantitative yield. When *p*-diacid chlorides were used, 0.4–1.0 g of lithium chloride was added before the amine addition.

Thermal Cyclodehydrations. Thin films of the poly(arylene acyloylamidoximes) were cast from 5% solutions of the polymer in DMAc (containing 5% lithium chloride for polymers IX and X). A sample of the film was placed in a polymer tube, connected to a vacuum pump at 0.1 mm pressure, and heated in a vapor both at the desired temperature for the desired length of time.

Solution Cyclodehydrations. A solution of 1.0 g of poly(arylene acyloylamidoxime), 8.0 g of lithium chloride for polymers IX and X, and 100 ml of DMSO or amide solvent was heated to 115–120° for 3 days and 150° for 2 hr. The resulting precipitated poly(arylene-1,2,4-oxadiazole) was washed with water and methanol in a blender and then dried at 80° for 16 hr in a vacuum oven. Yields were 95–100%.

Model Compounds. Condensations of appropriate monofunctional compounds with the diamidoximes or diacid chlorides were carried out by methods similar to those used for polymerizations. Cyclodehydrations were carried out either by heating the powders in evacuated polymer tubes, whereupon the 1,2,4-oxadiazole sublimed, or by heating solutions of the powders, whereupon the 1,2,4-oxadiazole precipitated under specific conditions of temperature and concentration.

Thermogravimetric analyses were obtained on a Du Pont 950 thermogravimetric analyzer at a heating rate of 5°/min.

Anomalous Polymerization Mechanisms. I. The Aqueous Acrylic Acid Dead End

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ABSTRACT: The polymerization of aqueous acrylic acid by potassium persulfate at 100° results in a limiting (dead-end) polymer yield which does not conform to the Tobolsky dead-end equation for the classical polymerization mechanism. Over the monomer concentration range $[M]_0 = 0.01–0.77\ M$, the relation between original initiator concentration, $[I]_0$, and residual fraction of unpolymerized monomer, U, is given by $[I]_0 = 0.00185\{\text{arc Tan}\ (60[M]_0) - \text{arc Tan}\ (60[M]_0U)\}$. By development of a *generalized dead-end theory*, it has been shown that the form of the empirical relation corresponds to dominance of a first-order termination reaction and to an effective kinetic competition between propagation and termination reactions for monomer-containing radicals which is of zeroth order with respect to radical concentration and of *second* order with respect to monomer concentration. The kinetic competition is much less favorable to termination for first stage (monomer-free) radicals and evidence for termination of these radicals is obtainable only below 0.01 M monomer concentrations. The mathematical analysis also provides a measure of the net monomer-consuming efficiency of the aqueous persulfate ion. The value obtained is unexpectedly high, but would be consistent with the presence of a *radical-proliferation process.*

The Empirical Dead-End Equation. The term *dead-end polymerization* was coined by Tobolsky[1] to characterize radical-chain polymerizations in which the reaction stops significantly short of exhaustion of the monomer. By integration of the classical rate equation[2] for radical-induced polymerization, he obtained the expression given by eq 1 for a limiting value of the monomer concentration in unlimited time. Satisfactory agreement with eq 1 was obtained for measurements

$$2k_p(f/k_T''k_d)^{1/2}[I]_0^{1/2} = \ln [M]_0/[M]_\infty = -\ln U = -\ln (1 - Y) \quad (1)$$

on styrene and isoprene.[3]

Aqueous acrylic acid solutions may be refluxed for many hours without appreciable change, but rapid polymerization is initiated by the addition of small quantities of potassium persulfate, presumably due to rapid dissociation of the persulfate anion into radicals under these conditions.[4] At 100° the polymerization ceases well within 1.5 hr after the persulfate addition,

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(1) A. V. Tobolsky, *J. Amer. Chem. Soc.*, **80**, 5927 (1958).

(2) P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p 114. The notation used in the present paper follows Flory with some modifications and necessary amplifications. The significance of the symbols in eq 1 is as follows: $[M]$ = concentration of unreacted monomer; $[M]_0$ = initial value; $[M]_\infty$ = limiting value; $U = [M]_\infty/[M]_0$ = limiting value of unpolymerized monomer fraction; $Y = 1 - U$ = limiting value of polymer yield fraction; $[I]$ = concentration of unreacted initiator; $[I]_0$ = initial value; f = initiator efficiency; k_d = rate constant of first-order primary cleavage of the initiator; k_p = the specific rate of propagation; k_T'' = the sum of the specific rates, k_{Tc}'' and k_{Td}'' of combination and disproportionation of the radicals. The double prime distinguishes these second-order termination rate constants from others to be introduced later.

(3) R. H. Gobran, M. B. Berenbaum, and A. V. Tobolsky, *J. Polym. Sci.*, **46**, 431 (1960); *Thiokol Magazine*, **3**, 5 (1964).

(4) I. M. Kolthoff and I. K. Miller, *J. Amer. Chem. Soc.*, **73**, 3055 (1951).