

Properties of Copolymers Derived from 2,5-Dimethylterephthalamidoxime and Cyclodehydration to Copoly(1,3-arylene-1,2,4-oxadiazole)s

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ABSTRACT: A series of copoly(1,3-arylene-1,2,4-oxadiazole)s was synthesized by thermal cyclodehydration of copoly(isophthaloylamidoxime)s, which were prepared by solution condensation from various mixtures of 2,5-dimethylterephthalamidoxime (DTD) and isophthalamidoxime (ID) with terephthaloyl chloride (TPC). The precursor copolymers containing mole ratios of 20% or more of DTD were soluble in *N,N*-dimethylacetamide (DMAc). Thermal properties of copoly(1,3-arylene-1,2,4-oxadiazole)s were investigated, and the effects of the methyl side groups are discussed. The introduction of dimethyl substituent improved solubility of copoly(1,2,4-oxadiazole)s greatly but lowered thermal resistance. All of the copolymers were found to be amorphous and glass transition could not be observed.

KEY WORDS Solubility / Thermal Stability / Heteroaromatic Copolymers / Copoly(1,2,4-oxadiazole) / Cyclodehydration / Isophthalamide Dioxime / 2,5-Dimethylterephthalamide Dioxime /

Since Tiemann and Küger suggested that 3,5-diphenyl-1,2,4-oxadiazole was exceptionally stable to thermal, oxidative and hydrolytic degradation,¹ several polymers containing 1,2,4-oxadiazole ring units have been synthesized by intramolecular cyclodehydration of the corresponding precursor poly(acyloylamidoxime)s.²⁻⁶ But all of the resulting polymers were infusible and only soluble in concentrated sulfuric acid. Recently much endeavor has been made to improve the processibility of high-temperature polymers by means of introducing flexible side branches onto stiff main chain including heteroaromatic polycondensates.⁷⁻¹⁰ In a previous paper we reported the synthesis of homo- and copoly(1,4-arylene-1,2,4-oxadiazole) derived from 2,5-dimethylterephthalamidoxime (DTD), and demonstrated improvement in solubility.¹¹

In this article, a series of copoly(1,3-arylene-1,2,4-oxadiazole)s was synthesized by cyclodehydration of copoly(amidoxime)s prepared from DTD and isophthalamidoxime (ID) instead of terephthalamidoxime (TD) as shown in Scheme 1, and their thermal properties were evaluated.

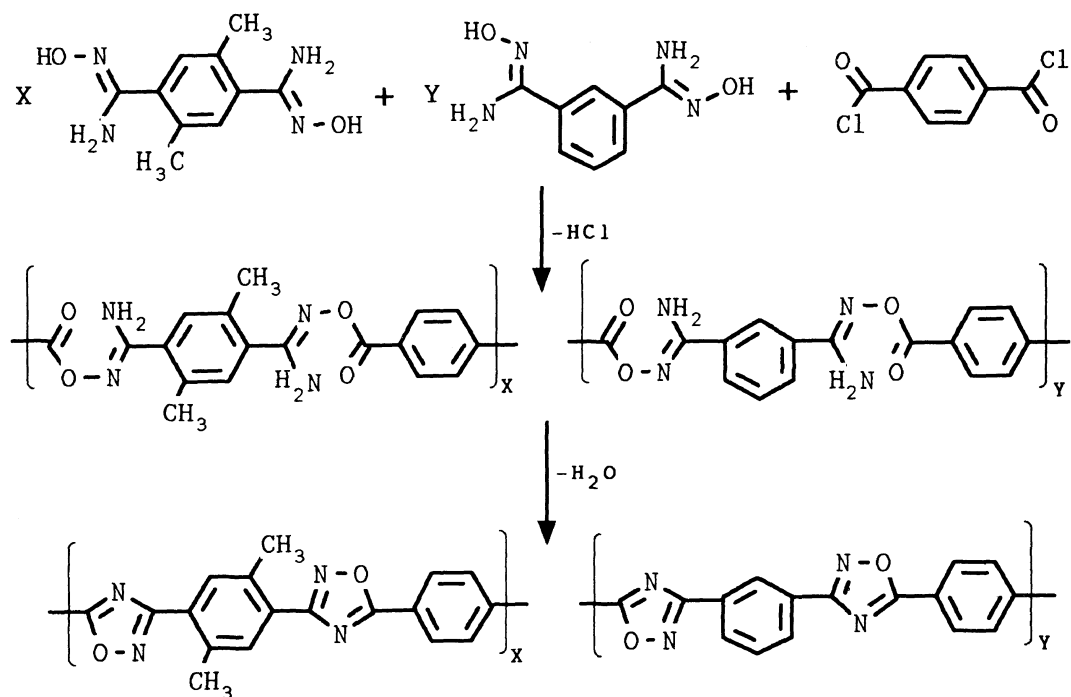
EXPERIMENTAL

Materials

DTD or ID was prepared as described by us¹¹ or others.^{6,12} *N,N*-Dimethylacetamide (DMAc) was purified by usual method. The other reagents were commercially available and used as received.

Polycondensation

Terephthaloyl chloride (5 mmol) was dis-



Scheme 1. Synthetic route to the copoly(1,3-arylene-1,2,4-oxadiazole)s.

solved in 10 ml of dry DMAc. This solution was added dropwise under a nitrogen atmosphere to a vigorously stirred solution of 0.5 mmol mixture of DTD and ID in dry 10 ml of DMAc. The reaction was allowed to proceed overnight at room temperature, and then the reaction mixture was heated to 60°C for another one hour. The composition of the bisamidoximes mixture was varied from DTD/ID=0/10 mol/mol to DTD/ID=10/0. For the homopolymer (DTD/ID=0/10), the reaction mixture was poured into excess acetone and the precipitate was collected by filtration. For the copolymers, the precipitate was obtained by removal of the solvent under reduced pressure. All the precipitated products were washed with water and acetone and dried at 80°C in vacuum.

Cyclodehydration

All the copoly(amidoxime)s were finely powdered by mortar and pestle. The powderic

sample was transferred to a small test tube, which was then immersed in an oil bath, connected to a vacuum pump at 0.1 Torr pressure and heated at 200°C for 48 h.

Characterization of the Copolymers

Solution viscosities of the polymers were measured at 30°C using a Ubbelohde-type viscometer. IR spectra were obtained with KBr pellets on a Perkin Elmer IR spectrometer. Differential scanning calorimetry (du Pont 910 DSC) and thermogravimetry (Perkin Elmer Delta Series TGA 7) measurements were performed at a heating rate of 20°C min⁻¹ under a nitrogen atmosphere.

RESULTS AND DISCUSSION

In addition to the previously described copoly(1,4-arylene-1,2,4-oxadiazole)s,¹¹ new copoly(1,3-arylene-1,2,4-oxadiazole)s were synthesized by the cyclodehydration of copoly-

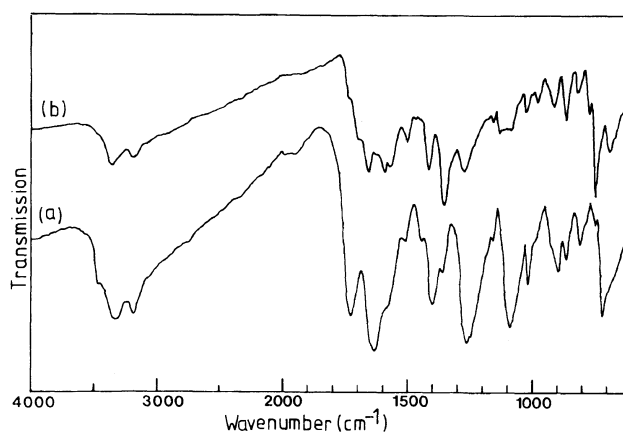


Figure 1. IR spectra of the (a) IA-2/8 and (b) IC-2/8 copolymers.

Table I. Monomer feed ratio of DTD/ID in the polycondensation with TPC and properties of the copoly(amidoxime)s

Polymer ^a code	DTD/ID ratio	η_{inh}^b	Solubility ^c in DMAc	$T_i/^\circ\text{C}^d$
	mol/mol			
IA-0/10	0/10	0.32	×	190
IA-2/8	2/8	0.29	△	176
IA-4/6	4/6	0.32	●	176
IA-6/4	6/4	0.20	○	154
IA-8/2	0/2	0.14	○	154
IA-10/0	10/0	0.12	○	172

^a Total [bisamidoxime]/[TPC] = 1/1 mol/mol.

^b Measured from 0.1 gdl⁻¹ solution in DMAc/LiCl = 95:5 (w/w) at 30°C.

^c ×, insoluble; △, swellable; ●, partially soluble; ○, completely soluble.

^d Initial weight-loss temperature determined by DTG.

(amidoxime)s, which were easily prepared by the solution polycondensation of a mixture of DTD and ID and terephthaloyl chloride (TPC) used at the monomer feed ratio shown in Table I. ID was used to make solubility even better. For property measurement in a more extended range of copolymer composition, homopolymers which were reported earlier by us (IA-10/0)¹¹ and others (IA-0/10)⁶ were re-prepared as shown in Table I. The homopolymer IA-0/10 was insoluble in the reaction

solvent DMAc and precipitated during the polycondensation, whereas copolymers IA-2/8—8/2 remained in solution.

All the obtained copoly(amidoxime)s were soluble in a solution of DMAc containing 5% lithium chloride by mass at room temperature. The same result was obtained previously by us from the copoly(amidoxime)s derived from TD.¹¹ Furthermore, copolymers IA-6/4 and IA-8/2 were completely soluble in DMAc in the absence of lithium chloride (Table I). Therefore, IA-copolymers generally had better solubility than TD-based copolymers which were practically insoluble in the solution of DMAc without LiCl.¹¹ The good solubility characteristics of IA-copolymers are attribute to disturbance of the main chain packing by introducing of kinked structure 1,3-phenylene unit into polymer backbone. Moreover, the possible positional isomerism of dimethyl group in phenylene unit along the chain and random linking mode of unsymmetrical oxadiazole toward 1,3-phenylene unit lead to a large increase in entropy. The solution viscosities of the copoly(amidoxime)s were rather low, ranging from 0.12 to 0.32 (Table I). No particular efforts were made to optimize the polymerization conditions in order to obtain high molecular weight (MW) polymers, because it has been already reported that no

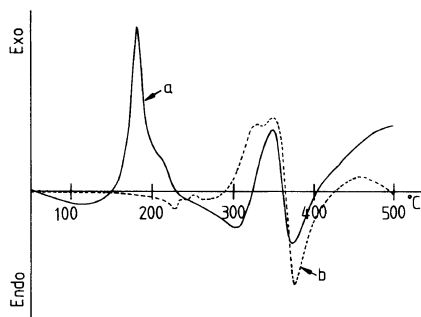


Figure 2. DSC thermograms of the (a) IA-8/2 and (b) IC-8/2 copolymers.

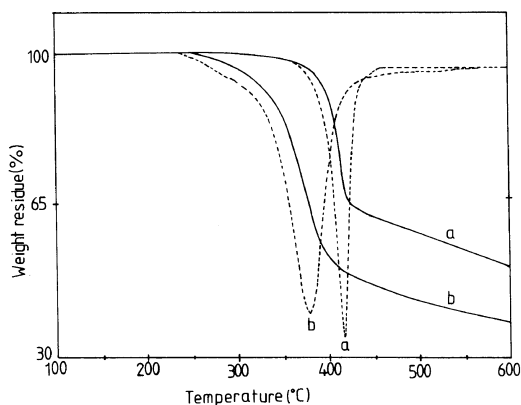


Figure 3. TGA (solid line) and DTG (dashed line) pyrograms of the (a) IC-0/10 and (b) IC-8/2 copolymers.

improvement in thermal stability was achieved at higher MW 1,2,4-oxadiazole polymers.⁶

The structures of copoly(amidoxim)s were identified from IR spectrum (Figure 1(a)) and their thermal properties were evaluated from DSC (Figure 2(a)) and differential thermogravimetry (DTG) methods (Table I). Figure 1(a) shows absorption bands at 3350 cm^{-1} and 3490 cm^{-1} (ν_{NH}), at 1735 cm^{-1} ($\nu_{\text{C=O}}$), and at 1618 cm^{-1} ($\nu_{\text{C=N}}$). The small peaks at 1360 cm^{-1} and 1150 cm^{-1} are assigned to methyl vibration. In Figure 2(a), the exothermic peak at 181°C , inflection of endothermic peak at 305°C and another exothermic peak at 347°C are observed. DSC analysis indicated that the intramolecular cyclization reaction took place

at about 200°C to 305°C , and the decomposition of the polymer occurred around $305\text{--}347^\circ\text{C}$. Unfortunately, sufficient experimental data to explain the strong exothermic absorption at 181°C are not yet available but a detailed investigation is underway at present. However, the DTG data in Table I show that the intramolecular ring closure reaction starts to take place at $154\text{--}190^\circ\text{C}$. In order to obtain poly(1,2,4-oxadiazole)s, the powder sample of all copoly(amidoxim)s was heated at 200°C under vacuum for 48 h.

Cyclodehydration of poly(amidoxim)s brought naturally change in polymer structure. This structural change was confirmed from IR spectrum, as shown in Figure 1(b). A big difference between IR spectra before and after cyclodehydration at 200°C for 48 h was observed. The formation of 1,2,4-oxadiazole ring was confirming by the appearance of a new C=N absorption band at 1575 cm^{-1} with remarkable decrease of the carbonyl absorption band at 1735 cm^{-1} as well as ν_{NH} band at 3350 cm^{-1} . Upon cyclizing, the ester carbonyl group condensed with the amino group leading to dehydration, and the applicable absorption peaks weakened. A fraction of these copolymers was then heated for longer time periods at the same temperature (200°C) but the IR spectrum did not change. These results suggest that cyclization was completed at 200°C , whereas a small amount of amidoxime end group was cleaved into an amide group.^{2,6}

None of copoly(1,2,4-oxadiazole)s gave rise to noticeable transition before decomposition on DSC analysis (Figure 2(b)). It is known that the fully aromatic polyetherpoly-1,2,4-oxadiazole has no melting point,² because it decomposes before melting. After DSC measurements it is believed that the homo- (IC-0/10) and all copolymers are amorphous. The random existence of a bent structure in the polymer backbone certainly would hinder crystallization. In spite of repeated heating and cooling experiments in DSC, no glass transition could be detected at all. Perhaps the segmental

Table II. Thermal pyrolysis behavior of copoly(1,2,4-oxadiazole)s^a

Polymer ^b code	Mole% DTD in monomer feed	T_i /°C ^c	T_{50} /°C ^d
IC-0/10	0	322 (373)	600
IC-2/8	20	303 (357)	413
IC-4/6	40	290 (355)	385
IC-6/4	60	275 (303)	435
IC-8/2	80	268 (298)	413
IC-10/0	100	260	375

^a Values in parentheses are T_i for copoly(1,4-arylene-1,2,4-oxadiazole)s.¹¹

^b Sample obtained after cyclized at 200°C for 48 h.

^c Initial decomposition temperature.

^d Temperature at 50% weight loss.

motion of the chain may be greatly hindered due to the presence of a dimethyl- or 1,3-phenylene unit and also because π -electrons are delocalized over the whole chain which therefore behaves like a rigid rod.

In Figure 3, TGA pyrograms of copoly(1,2,4-oxadiazole)s are reproduced. The TGA pyrogram shows that the thermal stability of the copolymer was reduced with increase of DTD concentration in the monomer feed. The effect of DTD concentration on T_i (the initial decomposition temperature) and T_{50} (the temperature at which weight loss reaches 50%) is summarized in Table II. For comparison, the values of T_i for copoly(1,4-arylene-1,2,4-oxadiazole)s, reported by us,¹¹ are also included in Table II. T_i decreased gradually with increasing DTD concentration in the monomer feed, whereas T_{50} of the copolymers decreased drastically and varied with the DTD concentration. This shows that the 2,5-dimethyl-1,4-phenylene unit in the homo- or copoly(1,2,4-oxadiazole)s lowered the thermal stability to a considerable degree, even when its content was quite low. It is interesting to compare the thermal stability of copoly(1,3-arylene-1,2,4-oxadiazole)s with that of copoly-

(1,4-arylene-1,2,4-oxadiazole)s. The latter copolymers have higher T_i values than the former as a whole (Table II). The low values of T_i for the former copolymers indicate the poor thermal stability of copolymers. The only difference of structures between two the types of copolymers is the substitution position of the phenylene moiety. Although the thermal degradation mechanism of such polymer has not been studied in detail, it appears that steric hindrance could reduce the thermal stability of the copolymers. In spite of this lowering in thermal resistance, the advantageous effect of the two methyl substituents and bent structure lies in improved solubility as mentioned in Table I.

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