Polymer Bulletin 20, 359–364 (1988)

Polymer Bulletin

Polymerization of terminal diynes by Niobium(V) catalysts

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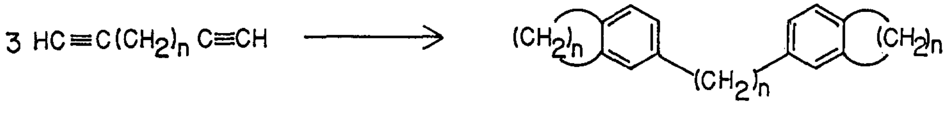
Summary

Terminal diynes of formula $HC{\equiv}CH(CH_2)_nC{\equiv}CH$ (n = 4,6,8), and 1,4-diethynylbenzene were polymerized by the cyclotrimerization catalyst $NbCl_5$. The new materials were characterized by nmr spectrometry and molecular weight measurements, and possess very high thermal degradation properties.

Introduction

Niobium(V) and tantalum(V) halides are known to be efficient cyclotrimerization catalysts for terminal acetylenes [1,2,3]. We reported the reaction of $HC{\equiv}C(CH_2)_nC{\equiv}CH$ (n = 2,3,4) as promoted by $NbCl_5$ to give trimeric molecules, as shown below [4].



Where n = 2, the product is 1,2-bis(benzocyclobutenyl)-ethane, which is an important crosslinking agent as well as a monomer for homopolymerization. The benzocyclobutane trimer was obtained in 90% yield, which is the highest reported to date. We observed that in α,ω-diynes where n = 3 and 4, the trimeric molecules 1,3-bis(benzocyclopentenyl)propane and 1,4-bis(benzocyclohexenyl)butane were obtained, although in lower yields; accompanying the reaction of these monomers was the production of polymers composed of 1,2,4- and 1,3,5-trisubstituted benzenes linked by $(CH_2)_3$ and $(CH_2)_4$ chains. We have now extended this reaction to terminal diynes where n = 6 and 8, and have found that polymers are formed exclusively.

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This paper reports the synthesis and properties of the new polymeric materials made from the cyclotrimerization of α,ω-diynes.

Experimental

Starting materials and solvents. All alkynes were purchased from either Farchan or Wiley and were purified by distillation over molecular sieves. 1,4-Diethynylbenzene was sublimed before use. Niobium(V) and tantalum(V) chlorides were obtained from Aldrich and used as received. Tetraphenyltin was recrystallized from CCl_4. Toluene was distilled over a sodium hydride dispersion and benzene over lithium aluminum hydride under an inert atmosphere of argon or nitrogen.

Physical methods. ^1H NMR studies were carried out on a Varian VXR-300 or Varian FT-80A spectrometer. Solid state ^{13}C NMR spectra were taken on a Chemagnetics CMC-200 spectrometer. Infrared spectra were recorded on a Perkin-Elmer 710B spectrophotometer. Molecular weights were determined by gel permeation chromatography using a polystyrene standard. TGA and DSC measurements were taken on a Dupont 1090 instrument.

Synthesis of the Polymers. The polymerization of 1,7 octadiyne, 1,9-decadiyne, 1,11-dodecadiyne, and 1,4-diethynylbenzene were all carried out in a similar fashion. Therefore only the reaction of 1,9-decadiyne will be given in detail.

A two-necked flask fitted with a rubber septum and gas adapter was placed in a glove bag in a nitrogen atmosphere and the catalyst $NbCl_5$(0.075 g, 0.27 mmol) and the cocatalyst $Sn(C_6H_5)_4$ (0.118 g, 0.27 mmol) were weighed in the flask. The gas adapter was replaced by a reflux condenser, and 40 ml of toluene was injected through the septum. The contents of the flask were warmed to 65°C in an oil bath, and 1,9-decadiyne (2.5 ml, 15 mmol) was added dropwise, by means of a syringe, over 5-8 min. An immediate exothermic reaction took place and the reaction mixture changed color from deep red to black. The reaction mixture was stirred magnetically at 65°C for 5 hr, then poured into 400 ml of methanol, and stirred for several hr. The resulting polymer was collected by filtration and dried under high vacuum. The weight of the polymer was 1.98 g (about 100% yield, considering small mechanical losses), and after a second purification from toluene/methanol, 1.86 g (95%) of the final polymer was recovered.

Table 1 shows the preparation details of the polymerizations run on 1,7-octadiyne (1,7-OD), 1,9-decadiyne (1,9-DD), and 1,11-dodecadiyne (1,11-DDD). Some comments on the results of the polymerization are appropriate. In the case of 1,7-octadiyne, Table 1 reports only that portion of the polymer that is soluble in toluene; the remainder of the products, to account for the high conversion, was 1,4-bis(benzocyclohexenyl)butane. In the case of $TaCl_5$ as the catalyst, high conversions to polymers were obtained, but the products were gels and mostly insoluble. For the $NbCl_5$ or $NbCl_5/Sn(C_6H_5)_4$ catalysts, high conversions were obtained and the polymers contained little gel.

Table 1. Polymerization of $HC{\equiv}C(CH_2)_nC{\equiv}H$

Monomer	Catalyst	Solvent	T, °C,	Conversion %	Polymer * %
n = 4	a	Bz	55	88	50
	a	Tol	80	90-95	53
	b	Tol	80	100	63
	c	Tol	80	60	33
n = 6	a	Tol	65	100	80
	a	Bz	55	95	85
	b	Tol	65	100	95
	c	Tol	65	100	20
	c	Bz	55	100	5
n = 8	a	Bz	55	95	80
	a	Tol	65	90	85
	b	Tol	65	100	95
	c	Bz	55	100	0
		Tol	65	100	5

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*% of polymer soluble in toluene; a = $NbCl_5$; b = $NbCl_5/Sn(C_6H_5)_4$; c = $TaCl_5$; Monomer: MCl_5 = 50:1; Bz = benzene; Tol = toluene

The product from the polymerization of 1,4-diethynylbenzene was totally insoluble in common organic solvents. This polymer was studied by DSC and ^{13}C (solid state) measurements.

Results and Discussion

Table 2 shows molecular weight data and Table 3 gives the physical and thermal properties for the polymers.

Table 2. Molecular Weights of the Polymers

Polymer	Catalyst	Solvent	Molecular Weights Mw x 10^3	Mn/Mn
poly(1,7-OD)	a	Bz	1.38	2.88
	b	Tol	1.34	3.8
poly(1,9-DD)	a	Bz	33.6	8.5
	a	Tol	35.4	8.2
	b	Tol	38.7	9.7
	c	Tol	30	6.4
poly(1,11-DDD)	a	Tol	27.3	6.1
	b	Tol	36	6.9

a = $NbCl_5$; b = $NbCl_5/Sn(C_6H_5)$; c = $TaCl_5$; Bz = benzene; Tol = toluene

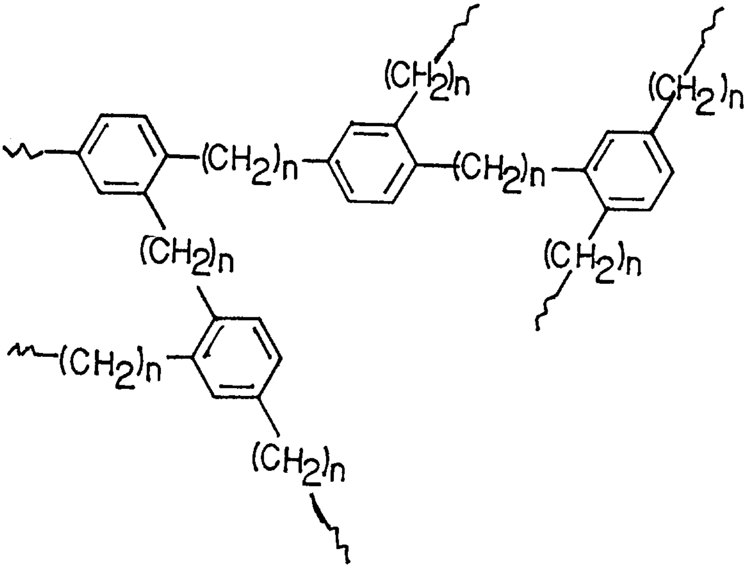
Table 3. Physical and Thermal Properties of the Polymers

Polymer	Catalyst	Physical Appearance	Tg, °C	TGA Wt. Loss in N_2(air) °C 10%	50%
poly(1,7-OD)	a	Viscous Tar	-	-	-
poly(1,9-DD)	a	Yellow-brown powder	18	465 (465)	500 (480)
	b	Brown elastomer	16	450	500
poly(1,11-DDD)	a	Yellow-brown elastomer	15	470	500
	b	Yellow-brown elastomer	14	445	480

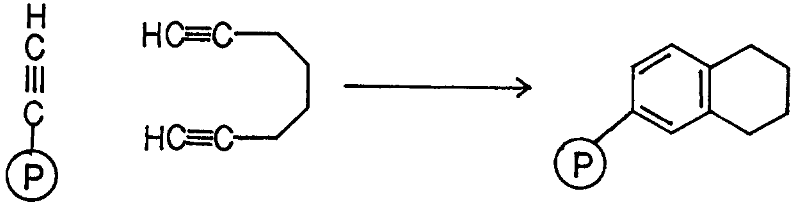
a = $NbCl_5$; b = $NbCl_5/Sn(C_6H_5)_4$

The ^1H NMR spectra of the polymers show fairly narrow lines for poly(1,7-OD), where the molecular weight is low.

Besides the aromatic proton signals (δ6.75-7.1, m, 1H), aliphatic ^{1}H signals are observed as two equal doublets (δ2.55 and 28, 2H, and δ1.65 and 1.8, 2H), indicative of the two isomers of the benzene substitution pattern (1,2,4- and 1,3,5), as pointed out earlier in trimerization of substituted acetylenes. Poly (1,9-DD) shows broader signals, and the aliphatic region exhibits different relative intensities, as expected: δ6.5-7.0, aromatic, m, 1H; δ2.6 and 2.45, 2H; δ1.5 and 1.3, 4H. The spectrum of poly (1,11-DDD) shows aromatic protons at δ6.7=7.0, m, 1H, and aliphatic signals at δ2.5, s, b, 2H, and δ1.5 and 1.2, 6H. These spectra are in accord with the expected structure of the polymers as shown below. Infrared spectra also support the presumed structure of the polymers; only aromatic and aliphatic CH absorbances are observed, and there is a complete absence of acetylenic C-H and C≡C bands.



The molecular weight of poly (1,7-OD) is low because the short length of the -CH$_2$- chain allows for a self-capping process to produce benzocyclohexene ends.



Poly (1,9-DD) and poly (1,11-DDD) show much higher molecular weights and much broader polydispersities than poly (1,7-OD), since the end-capping mechanism would be absent with these monomers.

The TGA curves show very high thermal degradation properties for these polymers, and also good resistance to air oxidation. Table 3 shows that a 50% weight loss does not occur until about 500°C, where the polymer degrades at the CH_2 groups. This was verified by studying the NMR spectra of the degradation products, which showed the benzene rings still intact.

The monomer β-diethynylbenzene was also polymerized by the Nb catalyst. The polymer is completely insoluble in common organic solvents, but we were able to obtain a solid state ^{13}C NMR spectrum and TGA data on it. The ^{13}C NMR spectrum shows major aromatic signals at δ150 and 180 ppm, both rather broad, and minor carbon signals from the acetylenic end groups at 75 and 85 ppm. The fact that the end groups are observed would indicate that the molecular weight is low. The TGA curves in air and N_2 were also measured; a 50% weight loss in N_2 was observed at about 590°C while that in air is 500°C. Once again, these compounds show very high thermal stability. In addition, since the polymer is completely conjugated, it should be a candidate for an electrically conducting species when properly doped.

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Accepted August 16, 1988 K