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The Fundamental Basis for Cyclopolymerization. II. The Relation of In-Plane-Deformation Vibrations of Terminal Methylene Groups of 1,6-Heptadienes to Polymerizability

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SUMMARY

A number of 4-substituted 1,6-heptadienes have been prepared and their infrared absorption characteristics compared with their polymerizability. This group of compounds included several N,N-diallylamides, diallylcyanamide, diallyl-(tricyanovinyl)-amine, diallylammonium bromide, diallylmethylphosphine oxide, diallylphenylphosphine oxide, diallylmethylphenylphosphonium bromide, and dimethyl-4-penteneamine. The frequencies of the in-plane-deformation vibration of the terminal methylene groups varied from 1411 to 1437 cm^{-1}. The higher frequencies were attributed to the electron withdrawal effect of the substituent in the 4 position. Those compounds having higher absorption frequencies also undergo polymerization more readily than those in the lower-frequency range. These correlations are presented as substantiating evidence for an intramolecular interaction in the monomers which can in part explain the facile but highly improbable cyclopolymerization mechanism.

INTRODUCTION

In the first paper of this series [1], evidence based upon a far ultraviolet study of a series of substituted silanes was presented in support of unconjugated chromophoric interactions in 1,6-heptadienes which are capable of undergoing cyclopolymerization, as was suggested in an earlier paper [2]. This paper deals with an infrared absorption study of certain 4-substituted 1,6-heptadienes, and an attempt to correlate the frequencies of in-plane-deformation vibrations of the terminal methylene groups with the

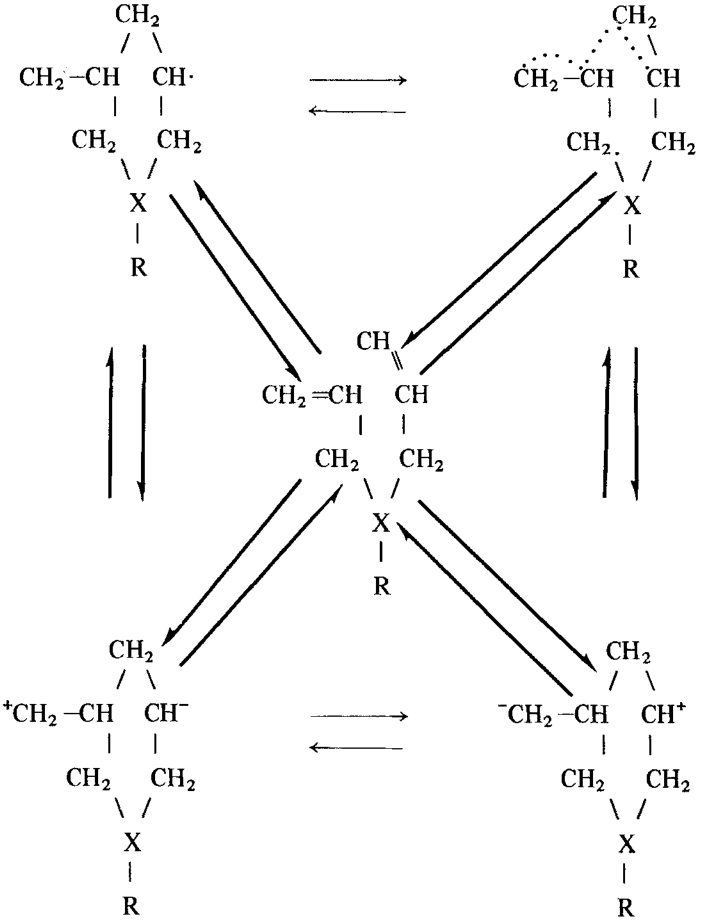


Table 1. Properties of the Compounds Prepared

Compound	% Conversion	Boiling point, °C/mm Hg	N_D^t	d^t	Retention time V.P.C. min/°C/ flow rate	Heat of vaporization, kcal/mole-deg[a]
Diallylformamide	65.2	96.5/19.0	$1.4693^{21.5°C}$	$0.9326^{21.5°C}$	4.12/196/20	13.2 ± 1
Diallylacetamide	85.7	100/16.3	$1.4693^{21°C}$	$0.9341^{21°C}$	4.96/200/20	13.5 ± 1.5
Diallyl-trifluoro-acetamide	80.5	81.1/25	$1.4130^{20.5°C}$	$1.138^{20.5°C}$	2.65/195/20	12.8 ± 1.5
Diallylpropionamide	80.0	102.0/12.6	$1.4685^{24°C}$	$0.9203^{24°C}$	6.30/200/20	13.6 ± 0.3
Diallylheptanamide	70.0	140.0/10.0	$1.4672^{22°C}$	$0.8977^{21°C}$	8.45/200/70	15.3 ± 0.5
Diallylnonanamide	55.4	144.0/10.0	$1.4664^{21°C}$	$0.8860^{21°C}$	10.30/200/20	13.7 ± 1.7

[a] Calculated from at least four different temperatures and pressures using the Clausius-Clapeyron equation.

Table 2. Attempted Polymerization of Diallylamides

Monomer	Monomer, g	Initiator Type[a]	Initiator Wt % of monomer	Solvent	Temp, °C	Time, hr	Conversion, approx. %[b]
Diallylformamide	0.93	BP	3.0	Benzene (50%)	85	95	Trace
	0.93	BP	3.0	–	85	95	Trace
	2.0	TBHP	0.5	–	80	144	Trace
	2.0	BP	1.0	–	80	144	Trace
	2.0	ABN	1.0	–	80	336	Trace
Diallylacetamide	0.93	BP	3.0	Benzene (50%)	85	95	–
	0.93	BP	3.0	–	85	95	Trace
Diallyl-trifluoroacetamide	1.14	BP	3.0	Benzene (50%)	85	95	3.5
	1.14	BP	3.0	–	85	95	6.4
	2.28	BP	1.1	–	80	49	3.0
	2.28	ABN	1.1	–	80	49	3.0
	2.85	ABN	3.0	–	73	25	5.0

Diallylpropionamide	1.11	BP	2.5	Benzene (50%)	85	95	–
	1.11	BP	2.5	–	85	95	–
	5.0	TBHP	1.0	Xylene (91%)	140	31	–
	6.0	TBHP	0.8	–	140	24	–
	10.0	TBHP	5.0	Xylene (80%)	140	48	–
Diallylheptanamide	0.90	BP	3.0	Benzene (50%)	85	95	–
	0.90	BP	3.0	–	85	95	–
Diallylnonanamide	0.89	BP	3.0	Benzene (50%)	85	95	–
	0.89	BP	3.0	–	85	95	–
Diallyl-tricyanovinylamine	0.425	BP	3.0	Benzene (70%)	85	160	4.0
	0.5	ABN	0.1	Benzene (85%)	75	127	3.0

[a] BP = benzoyl peroxide, TBHP = t-butylhydroperoxide, ABN = a,a′-diazoisobutyronitrile.

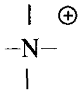
[b] Trace = 0.2-0.5%, – = < 0.2%.

electron-withdrawal effect of the 4 substituent and with the polymerizability of the compounds.

This study required the synthesis and characterization of a number of compounds of the type desired. Among these were the N,N-diallylamides of formic, acetic, trifluoroacetic, propionic, heptanoic, and nonanoic acids, and N,N-diallyl-N-tricyanovinylamine. The properties of these new compounds are reported in Table 1. Also acquired and studied were: diallylcyanamide (commercial), diallylmethylphosphine oxide [3], diallylphenylphosphine oxide [3], diallylmethylphenylphosphonium bromide [4], and dimethyl-4-penteneamine.

RESULTS AND DISCUSSION

It is well established that diallyldialkylammonium salts undergo cyclopolymerization to yield linear polymers containing little or no residual unsaturation [5]. Also, it has been shown that diallylamine salts undergo cyclopolymerization in a similar manner; however, the corresponding free amine is reluctant to do so [5]. Thus, it appears that the low electron density surrounding the 4 substituent, in this case the



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exerts a remarkable influence on the polymerizability of the compound. In an effort to establish the relation between monomer structure and the tendency to polymerize, the infrared spectral properties of a series of 1,6-heptadiene structures having substituents of widely differing electron-withdrawal power in the 4 position were determined. These compounds were also subjected to identical polymerication conditions to establish their relative polymerizability. The results of the polymerication study are recorded in Table 2, and the absorption frequencies of the in-plane-deformation vibration of the terminal methylene groups for these compounds are listed in Table 3.

It was predicted that the amides described above would undergo

Table 3. Absorption Frequency of In-Plane-Deformation Vibration of Terminal Methylene Group

Sample	Absorption, μ	Frequency, cm^{-1}	Sample thickness, mm
Diallylformamide	7.062	1416	0.015
Diallylacetamide	7.078	1413	0.015
Diallyl-trifluoroacetamide	7.038	1421	0.015
Diallylpropionamide	7.078	1413	0.015
Diallylheptanamide	7.078	1413	0.015
Diallylnonanamide	7.078	1413	0.015
Diallyl-tricyanovinylamine	7.052	1418	0.015
Diallylcyanamide	7.037	1421	0.015
Diallylammonium bromide	6.917[a]	1437[b]	KBr disk
Diallylmethylphosphine oxide	7.040[3]	1420	0.015
Diallylphenylphosphine oxide	7.057[3]	1417	0.015
Diallylmethylphenylphosphonium bromide	7.045[4]	1419	Melt
Dimethyl-4-pentene amine	7.080	1411[c]	Plates

[a] Value from R. Silas, Ph.D. Dissertation, University of Florida, June, 1954.

[b] LiF prism.

[c] NaCl prism.

homopolymerization via the cyclopolymerization mechanism with varying degrees of success. This prediction was based on the observations, as pointed out earlier, that diallyl quaternary ammonium halides do undergo cyclopolymerization while diallylamine does not. Also, other compounds, such as the diallylphosphorus compounds [3, 4] mentioned earlier and diallylphthalate [6], have been polymerized to soluble polymers by free radical initiators. Other workers have described soluble copolymers from 1,6-heptadiene systems, such as diallylalkylamine oxides and acrylonitrile [7], and a variety of other copolymer systems [8, 9].

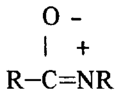
The conversions to polymer for the diallylamides as shown in Table 2 are approximate values only but may be taken as indicative of the polymerizability of the monomers in a homopolymerization system. The only samples which resulted in appreciable conversions were the tricyanovinyl and trifluoroacetyl derivatives. These two compounds contain groups which are among the most electron-withdrawing groups in the series. Diallylammonium bromide has previously been shown to give a high conversion to polymer [5]. Since trace quantities of polymer were obtained from the formyl derivative, the next most powerful electron-withdrawing substituent, there seems to be a definite correlation between the electron-withdrawing power of the substituent on the nitrogen atom of diallylamine and the polymerizability of the monomer. Thus, it is observed that the stronger the electron-withdrawing power of a substituent the more readily the monomer undergoes homopolymerization in a free radical system.

The proposed intramolecular interaction is supported by the work of Mikulasova and Hvrik [10a, b] in which they determined that the total activation energy for radical polymerization of diallyldimethylsilane is about 9 kcal/mole double bond less than that for allyltrimethylsilane; however, the reliability of these data has been questioned [10c]. Other evidence which supports this type of interaction is based on polymerization of nonconjugated diene systems, such as 2,5-dimethyl-1,5-hexadiene by metal alkyl coordination catalysts [11]. This study also included the mono-olefin, 2-methyl-1-pentene, which did not yield high-molecular-weight materials. The investigators considered both of these systems as 1,1-disubstituted ethylenes and suggested that the driving force afforded by the formation of the cyclic structure was responsible for the success in polymerization of the diene and the lack of success in the case of nono-olefin.

The absorption frequencies for the in-plane-deformation vibration of the terminal methylene group in the 1,6-heptadiene series appear to be somewhat anomalous for those compounds having strong electron-withdrawing substituents in the 4 position, as shown in Table 3. Bellamy [12] in his comprehensive text on infrared spectra assigns this group to the 1420-1410 cm^{-1} region and further reports: ". . . the band near 1415 cm^{-1} is usually strong in the infrared and is very stable in position, so that it serves as a useful guide in analysis. The substitution of $-CH_2OR$ and $-CH_2OCOR$ groups has little or no effect upon this frequency, but in case of acrylates and methacrylates it shows a slight fall to 1405 cm^{-1}."

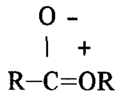
It will be observed from the values in Table 3 that there is a definite shift in the frequency of absorption in the series of 1,6-heptadiene compounds listed. This shift may be correlated well with the results from polymerization studies. It is seen that the shift to a higher absorption frequency for the group under consideration parallels the polymerizability of the monomer. Thus, the more readily the monomers undergo polymerization the higher the absorption frequency for the in-plane-deformation vibration of the terminal methylene group.

The shifts are not large in absolute magnitude, but the trend which is exhibited appears to be significant. This shift in frequency can probably best be explained by a combination of two electrical effects present in the molecules. These two effects are the inductive effects exerted through the chain and the mesomeric effect exhibited by the amide group in the sharing of the lone-pair electrons of the nitrogen with the carbonyl carbon atom. Thus, canonical forms such as



$$\begin{array}{c} O\ - \\ |\ \ + \\ R{-}C{=}NR \end{array}$$

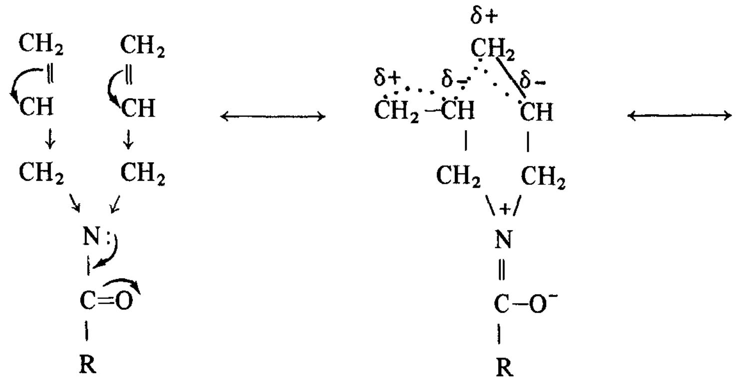
and

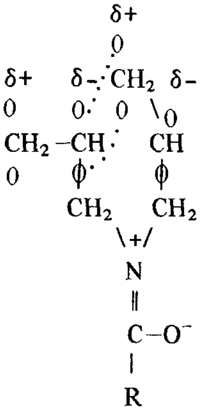


$$\begin{array}{c} O\ - \\ |\ \ + \\ R{-}C{=}OR \end{array}$$

will contribute to the structure of the amides. Bellamy [13] points out that this contribution is most marked with the amide type of compounds. The combination of these two effects, the mesomeric effect to give a positive charge or at least a partial charge on the nitrogen atom and the inductive effect to distort the electron cloud normally distributed between the terminal carbons, can be offered as plausible support for structures of possible forms supporting the proposed interaction between the two allyl groups.

Thus, the combination of the two electrical effects may be illustrated as follows:





The definite trend in the amide series, that of increasing polymerizability with decreasing basicity of the nitrogen atom, is further borne out by inclusion of the quaternary ammonium salt, which is the least basic of the series and the most polymerizable. Absorption occurs at the highest frequency in this compound.

EXPERIMENTAL

Preparation of Monomers

N,N-diallylformamide [14]. Formic acid (25 g, 0.54 mole) was added dropwise with stirring to diallylamine (50 g, 0.52 mole), and the reaction was allowed to stir for 1 hr. The mixture was then heated to remove excess reactants and the water formed during the reaction. The temperature was maintained at 150°C for 1 hr, and the residue was distilled at reduced pressure. The crude product was redistilled, and careful fractionation gave a clear, water-white liquid (48.9 g, 65.2%); bp, 81.5°C at 9.0 mm, 88.2°C at 12.4 mm, 93.0°C at 15.8 mm, 96.5°C at 19.0 mm; $n_D^{21.5}$, 1.4693; $d^{21.5}$, 0.9326; MR_D, 37.395, calculated 37.413; ΔH_V, 13,200 ± 1000 cal $mole^{-1}$ deg^{-1}; retention time, 4.12 min at 196°C; helium flow rate, 20 ml/min. Analysis: Calculated for $C_7H_{11}NO$: C, 67.16; H, 8.86; N, 11.19. Found: C, 67.34; H, 9.03; N, 11.04.

N,N-diallylacetamide [15]. Diallylamine (49 g, 0.5 mole) was added dropwise with stirring to acetic anhydride (51 g, 0.5 mole); the mixture was then reluxed gently for 24 hr. Unreacted materials and acetic acid were removed by distillation at atmospheric pressure, and the remaining crude product was distilled at reduced pressures. Fractionation gave a clear, water-white liquid (60.0 g, 85.7%); bp, 95°C at 12.7 mm, 98°C at 14.6 mm, 100°C at 16.3 mm, 101.4°C at 17.3 mm, 103.2°C at 19.0 mm; n_D^{21}, 1.4963; d^{21}, 0.9341; MR_D, 41.516, calculated 42.031; ΔH_V, 13,500 ± 1500 cal mole^{-1} deg^{-1}; retention time, 4.96 min at 200°C; helium flow rate, 20 ml/min. Analysis: Calculated for $C_8H_{13}NO$: C, 69.03; H, 9.41; N. 10.07. Found: C, 68.85; H, 9.64; N, 10.21.

N,N-diallyl-trifluoroacetamide. Diallylamine (50 g, 0.52 mole) was added dropwise to ethyl trifluoroacetate (75 g, 0.53 mole). The reaction mixture was protected by a Drierite tube and allowed to stand at room temperature for 1 week. The reaction mixture was fractionally distilled to yield a clear, water-white liquid (80.0 g, 80.5%) with a pungent, nauseating odor; bp, 71.3°C at 15.3 mm, 76.5°C at 20 mm, 81.1°C at 25 mm, 84.3°C at 30 mm; $n_D^{20.5}$, 1.4130; $d^{20.5}$, 1.138; MR_D, 42.342, calculated 42.031; ΔH_V, 12,800 ± 1500 cal mole^{-1} deg^{-1}; retention time, 2.65 min at 195°C; helium flow rate, 20 ml/min. Analysis: Calculated for $C_8H_{10}NOF_3$: C, 49.74; H, 5.22; N, 7.25. Found: C, 50.01; H, 5.21; N, 7.03.

N,N-diallylpropionamide. Diallylamine (44 g, 0.045 mole) was added dropwise with stirring to propionic anhydride (59 g, 0.45 mole) over a 1-hr period. The mixture was heated to reflux and maintained at reflux for 16 hr with stirring. On careful fractionation, the reaction mixture yielded a clear, water-white liquid (50.2 g, 80%), diallylpropionamide; bp, 110-111°C at 20 mm. Refractionation gave bp 86.0°C at 5.6 mm, 96.0°C at 9.5 mm, 102.0°C at 12.6 mm, 110°C at 19 mm; n_D^{24}, 1.4685; d^{24}, 0.9203; MR_D, 46.326, calculated 46.649; ΔH_V, 13,600 ± 300 cal mole^{-1} deg^{-1}; retention time, 6.30 min at 200°C; helium rate, 20 ml/min. Analysis: Calculated for $C_9H_{15}NO$: C, 70.55; H, 9.87; N, 9.14. Found: C, 70.61; H, 9.89; N, 9.32.

N,N-diallylheptanamide. Heptanoyl chloride (30 g, 0.20 mole), prepared by the method outlined by Shirley [16] by reaction of thionyl chloride and heptanoic acid, was added dropwise with stirring to diallylamine (40 g, 0.41 mole) in benzene (100 ml) over a 1-hr period. After addition was complete, the reaction mixture was heated to reflux and stirred for an additional 4 hr. The solid amine hydrochloride was removed by filtration, washed with 30 ml of benzene, and discarded. The filtrates were combined, the benzene was removed under reduced pressure, and the remaining crude product was fractionally distilled to yield a clear, water-white liquid (29.3 g, 70%), diallylheptanamide; bp, 143-144.5°C at 9.6 mm. Refractionation gave bp 140°C at 10 mm, 145°C at 12.4 mm, 150°C at 15.6 mm, 154°C at 18.4 mm; n_D^{22}, 1.4672; d^{21}, 0.8977; MR_D, 64.706, calculated 65.121; ΔH_V, 15,300 ± 500 cal $mole^{-1}$ deg^{-1}; retention time, 8.45 min at 200°C, helium flow rate, 70 ml/min; retention time, 9.06 min at 227°C, helium flow rate, 20 ml/min. Analysis: Calculated for $C_{13}H_{23}NO$: C, 74.59; H, 11.08; N, 6.69. Found: C, 74.66; H, 11.11; N, 6.72.

N,N-diallylnonanamide. Nonanoyl chloride (40 g, 0.28 mole), prepared by the same method as heptanoyl chloride above, was added dropwise with stirring to a benzene solution (100 ml) of diallylamine (63 g, 0.65 mole) over a 1-hr period. After addition was completed, the reaction mixture was heated to reflux and stirred for an additional 4-hr period. The solid diallylamine hydrochloride was filtered off, washed with 30 ml of benzene, and discarded. The two benzene portions were combined, and the benzene was removed under reduced pressure. The remaining crude material was fractionally distilled to yield a clear, water-white liquid (37 g, 55.4%), diallylnonanamide; bp, 101-102°C at 0.5 mm. Refractionation gave bp 137°C at 7.8 mm, 144°C at 10.0 mm, 151.5°C at 15.1 mm, 159.5°C at 20.4 mm; n_D^{21}, 1.4664; d^{21}, 0.8860; MR_D, 74.274, calculated 74.357; ΔH_V, 13,700 ± 1700 cal $mole^{-1}$ deg^{-1}; retention time, 10.30 min at 200°C; helium flow rate, 20 ml/min. Analysis: Calculated for $C_{15}H_{27}NO$: C, 75.89; H, 11.47; N, 5.90. Found: C, 75.89; H, 11.33; N, 5.96.

N,N-diallyl-N-tricyanovinylamine. The general procedure used was as outlined by McKusick et al. [17] for preparation of N,N-dialkyl-N-tricyanovinylamines. Diallylamine (7.6 g, 0.0785 mole) was added dropwise with stirring to tetracyanoethylene (10 g, 0.0780 mole) dissolved in tetrahydrofuran (200 ml). The addition rate was adjusted so that the temperature of the reaction mixture did not rise above 35°C. After addition was completed, the mixture was heated to reflux for a 3-hr period. The solvent was removed under reduced pressure to yield a black, viscous oil, soluble in acetone and ethanol, slightly soluble in benzene, and insoluble in water and pentane. All attempts to crystallize this material were unsuccessful. The crude reaction mixture was degassed at less than 0.1 mm for 24 hr. An attempt to sublime the product out of the crude mixture at 0.05 mm and 90°C was unsuccessful. A 5-g sample was deposited from a warm, saturated, benzene solution onto a chromatographic column prepared from benzene and activated alumina. Elution with 200 ml of benzene gave a clear, yellow solution. Attempts to precipitate a solid from the benzene solution by addition of nonsolvents or by cooling were unsuccessful. Evaporation of the benzene under reduced pressure yielded a yellow-red oil. The product was identified as diallyltricyanovinylamine by infrared, ultraviolet, and elemental analyses. An ethanol solution was used to determine the ultraviolet absorption spectrum: λ max, 3340 Å; ϵ, 14,300. Analysis: Calculated for $C_{11}H_{10}N_4$: C, 66.65; H, 5.09; N, 28.27. Found: C, 66.90; H, 5.38; N, 27.94.

All physical properties were determined on samples which were indicated to consist of a single component by gas chromatographic analysis. Gas chromatographic analyses were carried out on an Aerograph gas chromatographic instrument using helium as the carrier gas and a 5-ft Aerograph 150-A-1 column (silicone on five brick).

Polymerization Procedure

Weighed quantities of the reactants, and solvent if used, in 20-ml ampoules were flushed with dry nitrogen gas, and the ampoules were cooled in a dry ice-acetone mixture before being sealed off by use of an oxygen-methane torch. Polymerizations were carried out in an oven at the temperature and for the period of time indicated in Table 2. This procedure was followed in all of the polymerization attempts except those in which the initiator was t-butylhydroperoxide. In these experiments the samples were contained in a 100-ml tube fitted with a reflux condenser and with a standard taper ground-glass joint suitable for fitting into a refluxing xylene bath. In this way a constant temperature of 140°C was maintained during these runs.

The polymers were isolated by addition of the reaction mixture to a large excess of methanol. The methanol mixtures were then filtered through a medium-porosity sintered-glass filter. The filters were dried in vacuo for 24 hr and the increase in weight was taken as the yield of polymer in each case.

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