

High Pressure Polymerisation of Acetylenic Compounds

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Acetylenic compounds have been polymerised by heating at pressures up to 23.5 kbar in the absence of initiators. The products are either low melting or intractable solids. 2-Butyne copolymerises with tetramethylethylene and trimethylethylene. Propiolic acid gives carbon dioxide and a mixture of aromatic acids as well as an amorphous polymeric acid.

1. Introduction

Polymerisation of acetylenes is less well known than that of olefins, and although polymers and oligomers have been obtained under a variety of conditions^{1,2}, little has been published on high pressure polymerisations. It has been established³ that initiators have little effect on the high pressure liquid phase polymerisations of acetylenes although in some cases solid phase polymerisations are initiated by the application of a shear stress which possibly produces free radical centres.^{4,5} This paper reports the polymerisation of several acetylenes at pressures up to 23.5 kbar,^a generally in fluid systems and in the absence of initiators.

2. Experimental

Monomers were commercially available and were purified by distillation.

High pressure reactions were carried out in capsules immersed in the hydraulic fluid in the piston/cylinder apparatus described elsewhere.⁶ Capsules were made from lengths of gold tubing (0.1 mm × 12.7 mm i.d. or 0.1 mm × 5.0 mm i.d.) sealed by suitable end closures,⁶ which in the case of small capsules could consist of simple mild steel clamps. Gases and volatile liquids were distilled into a capsule through a short length of nickel tube (1 mm i.d.) which was silver-soldered at one end into the capsule end-closure while the other end was soft-soldered to a copper tube which was in turn connected via a metal-glass joint and condenser to a vacuum system. After filling, the capsule was sealed by pinching off the nickel tube with a hand-operated lap welding tool.

Molecular weights were measured in toluene solutions in a Mechrolab Vapour Phase Osmometer. Infrared spectra were taken as KBr discs on a Perkin Elmer grating

^aThroughout this paper 1 kbar = 987 atm = 100 MN/m².

spectrophotometer Model 457. Analyses were carried out by the Microanalytical Laboratory, Chemical Standards Division, N.P.L.

3. Results and Discussion

High pressure polymerisations of acetylenes are violently exothermic and frequently only carbonaceous products were obtained. In some cases where the run-away reactions were monitored by DTA⁷ the temperature rose rapidly by several hundred degrees and the outsides of the recovered capsules bore traces of soot produced by pyrolysis of the hydraulic fluid. In general it is necessary either to modify the rate of reaction by using an inert diluent or to carry out the polymerisation in small diameter capsules, thus increasing the surface area/volume ratio and facilitating the dissipation of the heat reaction.

The conditions reported (Table I) are those at which the reactions were carried out and it is possible that polymerisations would have taken place under milder conditions. It appears that monosubstituted acetylenes are more readily polymerised than the disubstituted compounds, presumably owing to the reactivity of, and reduced steric hindrance about, the $\equiv\text{CH}$ group. The completeness of the reactions is indicated by the absence of the $\text{C}\equiv\text{C}$ stretching absorptions ($\sim 2100\text{ cm}^{-1}$ monosubstituted, $\sim 2200\text{ cm}^{-1}$ disubstituted) from the infrared spectra of the polymers.

The tendency of acetylenes to cyclise is well known² and the production of cyclic oligomers, in particular aromatic compounds, in these high pressure reactions would be expected. In fact in only two cases, perfluoro-2-butyne and propiolic acid, has any evidence of small ring formation been found. Little evidence concerning the structures of the polymers obtained is available. It has been suggested⁸ that propiolic acid and some related compounds give ladder polymers when polymerised under pressure, and it is possible that such structures are formed during the polymerisations now reported, but in general the intractable nature of the polymers makes structural determinations difficult. Those which have been examined by X-ray diffraction have been found to be completely amorphous.

3.1. 2-Butyne

No polymerisation is observed at pressures below 10 kbar and temperatures up to 190 °C. At 23.5 kbar and 250 °C a brittle, pale yellow resin is obtained from this monomer alone (in a small capsule) or diluted with isopentane. The resin is insoluble in, and un-swollen by, all common organic solvents but melts to a clear yellow liquid at 369 to 70 °C *in vacuo*. It darkens in air above 180 °C and in a nitrogen atmosphere loses weight above 250 °C. Spectroscopic evidence for the structure of the resin is

consistent with a network of $\text{Me}-\text{C}-\text{C}-\text{Me}$ groups with a few isolated $\text{C}=\text{C}$

groups. The infrared spectrum shows strong absorption peaks due to aliphatic, mainly $-\text{CH}_3$, C-H bonds (2960, 2930, 2875, 1460, 1380 cm^{-1}) and broad minor peaks at

TABLE I. Polymerisation of acetylenes

Monomer	Polymerisation conditions			Analyses (%)		M.W. (V.P.O. in toluene solution)	Comments
	Pressure (kbar)	Temperature (°C)	Time (h)	Found (upper) Calculated (lower) C	H		
2-Butyne	23.5	250	21	89.0 88.9	11.0 11.1	—	M.p. 353–9 °C (vac).
2-Butyne [diluted with isopentane (1:1 v/v)]	23.5	250	24	88.7 88.9	11.6 11.1	—	
2-Butyne + trimethylethylene (2:1 molar)	23.5	250	20	87.55 87.6*	12.25 12.4*	1054 1068*	*Calc. for $[2C_4H_6.C_5H_{10}]_6$
2-Butyne + tetramethylethylene (10:1 molar)	23.5	250 (Temp. raised slowly during 3 h)	19	88.1 88.5*	11.7 11.5*	—	M.p. 344–8 °C (vac). *Calc. for $[10C_4H_6.C_6H_{12}]_n$
2-Butyne + tetramethylethylene (2:1 molar)	23.5	250	21	(a) Oil (14%) pumped off (Bath temp), 0.01 mmHg 87.0 86.6*	at 200 °C 13.2 13.3*	335 360 *	TME (6.7% recovered) *Calc. for $[2C_4H_6.3C_6H_{12}]$
				(b) Residue (66%) after pumping off oil 87.7 87.5*	12.5 12.5*	1147 1154*	*Calc. for $[2C_4H_6.C_6H_{12}]_6$
1-Butyne [diluted with isopentane (1:1 v/v)]	6–7.5	100–200	5	92.0 88.9	6.2 11.1	—	Dark viscous liquid
2-Hexyne	23.5	255	20	83.3 87.8*	11.5 12.2*	724 738*	M.p. < 90 °C *Calc. for $[C_6H_{10}]_9$
Perfluoro-2-butyne	23.5	250	30	29.3 29.6	— —	—	M.p. > 360 °C
Propargyl alcohol (prop-1-yn-2-ol)	23.5	100	14	63.9 64.3	6.7 7.15	—	M.p. > 360 °C
Propiolic acid (propynoic acid)	23.5	100	18	55.8 55.0 54.5 54.8*	4.2 4.1 4.3 3.3*	—	M.p. > 360° *Calc. for $[C_7H_5O_4]_n$

~ 1700 and 1000 cm^{-1} possibly due to $\text{C}=\text{C}$. A specimen dispersed in KBr showed no ultraviolet absorption peaks in the range 200 to 400 nm, indicating the absence of conjugated $\text{C}=\text{C}$ and aromatic bonds.

It is interesting to compare the polymer from 2-butyne with one obtained from 1,3-butadiene. The diene was heated in isopentane solution (1:1 v/v) and the reaction was monitored by DTA. Polymerisation commenced at $80\text{ }^\circ\text{C}$ at 8.5 kbar and was complete after heating to $150\text{ }^\circ\text{C}$ and 14 kbar over 2 h. The infrared spectrum of the rubbery polymer obtained shows, besides absorptions due to CH_2 groups (2920 , 2840 , 1440 cm^{-1}), absorptions due to olefinic groups at 3075 ($=\text{CH}_2$), 1680 ($\text{C}=\text{C}$), 965 (CH) and 910 cm^{-1} (CH_2). In addition, GLC analyses of the pyrolysis ($700\text{ }^\circ\text{C}$) products of the two polymers show different distributions of the break down products among the low molecular weight fragments (C_2 to C_4) and the butadiene polymer gives more products with longer retention times. It would seem that there is little tendency for 2-butyne ($\Delta G_f^\circ = 44.725\text{ kcal/mol}$) to isomerise to 1,3-butadiene ($\Delta G_f^\circ = 36.43\text{ kcal/mol}$) under the conditions of high pressure polymerisation.

2-Butyne copolymerises with trimethylethylene and tetramethylethylene in 2:1 molar ratios giving soluble polymers of indefinite (*c.* $100\text{ }^\circ\text{C}$) melting points. The small quantity of liquid copolymer obtained from 2-butyne-tetramethylethylene by heating the initial product is possibly produced by degradation of the 2:1 copolymer. As would be expected the 2-butyne-tetramethyl ethylene 10:1 copolymer is insoluble and resembles the 2-butyne homopolymer.

3.2. 1-Butyne

This monomer appears to be more readily polymerised than 2-butyne, but the low molecular weight, viscous liquids obtained are rich in carbon suggesting that some decomposition occurs. The infrared spectrum shows only absorptions due to aliphatic C-H bonds.

3.3. 2-Hexyne

Some hexyne was recovered after heating the undiluted monomer in a small capsule. The polymer, a low melting solid approximating to the monomer, shows only aliphatic C-H absorptions in the infrared spectrum.

3.4. Perfluoro-2-butyne

The polymerisation of this monomer, undiluted and in small capsules, was erratic and of five experiments, one gave the polymer, three gave only carbonaceous material, while in the fifth experiment the capsule split during the reaction and was found to contain polymer contaminated with oil in one part and carbonaceous matter in the other. The polymer is a brittle, amber, insoluble resin, density $\sim 2.0\text{ gm/cm}^3$, which does not melt below $390\text{ }^\circ\text{C}$ but which begins losing weight at $100\text{ }^\circ\text{C}$ and when heated in nitrogen at 375 , 570 , 640 and $690\text{ }^\circ\text{C}$ had respectively lost 20, 40, 60 and 100% of its original weight. The infrared spectrum of the polymer has a broad absorption band in the range 1150 to 1300 cm^{-1} (maxima at 1170 , 1190 , 1240 , 1260 cm^{-1}) and minor peaks

at 878, 710, 620 and 455 cm^{-1} , but no absorptions at higher frequencies. Examination mass-spectrographically (probe at $110\text{ }^{\circ}\text{C}$) gives little information on the structure of the polymer. The mass spectrum has numerous peaks including two corresponding to the trimer and the tetramer (Found, $M = 485.966, 647.963$; Calc for $\text{C}_{12}\text{F}_{18}$, $M = 485.969$; Calc for $\text{C}_{16}\text{F}_{24}$, $M = 647.962$). These may be breakdown products of the polymer but it is known^{9,10} that perfluoro-2-butyne is converted into hexabis (trifluoromethyl) benzene and to tetramers when heated at moderate pressures and the direct production of these at higher pressures would not be unexpected.

3.5 Propargyl alcohol (Prop-1-yn-1-ol)

The undiluted monomer is readily polymerised in small capsules at temperatures below *c.* $110\text{ }^{\circ}\text{C}$ to an infusible, insoluble resin. At higher temperatures carbonaceous materials are obtained. The high pressure polymerisation of this monomer under somewhat different conditions has been reported^{8,11} and two different structures have been suggested for the polymer. The infrared spectrum of the polymer obtained in the present experiments has a broad absorption attributable to $\text{C}=\text{C}$ bonds at 1670 cm^{-1} , and the relative intensities of absorptions due to the $\text{O}-\text{H}$ bond at 3000 to 3500, 1400 and 1030 cm^{-1} are reduced compared with those in the spectrum of the monomer. This is consistent with a structure containing linear chains of $-\text{CH}=\text{C}(\text{CH}_2\text{OH})$ -units cross-linked by addition of the OH groups to multiple bonds,¹¹ rather than the alternative ladder structure.⁸

3.6 Propiolic acid (propynoic acid)

This monomer undergoes a smooth reaction at 23.5 kbar in *c.* 8 ml lots provided the temperature does not exceed $100\text{ }^{\circ}\text{C}$. At 23.5 kbar and $80\text{ }^{\circ}\text{C}$ and at 10 kbar and $100\text{ }^{\circ}\text{C}$ the polymerisation is incomplete after 18 h. It is likely that the reaction at the lower pressure takes place in the liquid phase and at the higher pressure in the solid. At temperatures greater than $100\text{ }^{\circ}\text{C}$, even in the presence of an inert diluent, a vigorous reaction giving a carbonaceous product occurs, which in one case lead to an explosion which ruptured the high pressure vessel.

A distinctive characteristic of the high pressure transformation of propiolic acid is the production of carbon dioxide (*c.* 12.5% w/w; i.e. *c.* 1 mol CO_2 per 5 mol acid) identified by its infrared spectrum. It is well known that $\alpha\beta$ -acetylenic carboxylic acids are readily decarboxylated by heating,¹² but it might be expected that this reaction would be inhibited by the application of pressure. Other low molecular weight products formed in the transformation are aromatic acids (*c.* 11.5% w/w), isolated by ether extraction of the solid reaction products. The principal constituents of the mixture, identified by infrared spectroscopy, are isophthalic and benzene-1,3,5-tricarboxylic acids in approximately equimolecular amounts. Benzene-1,2,4-tricarboxylic acid could not be detected: distinctive absorption peaks at 1500, 770 and 595 cm^{-1} in the spectrum of this acid, but absent from the spectra of the 1,3- and 1,3,5- acids, are not present in the spectrum of the mixture of acids obtained from the reaction, but a very small quantity of phthalic anhydride was separated by sublimation of the mixture. It appears, therefore, that the molecules trimerise almost exclusively in

a head-to-tail configuration, and since no decarboxylation occurs when either 1,3,5- or 1,2,4- tricarboxylic acid is heated under pressure, the loss of carbon dioxide must occur during the cyclisation reaction leading to isophthalic acid.

The main product (*c.* 76%) of the reaction is an amorphous, flaky, brown material whose infrared spectrum shows only broad bands in regions characteristic of the carboxylic acid group (3300 to 2500, *c.* 1700, *c.* 1400 and *c.* 1200 cm^{-1}). Although small quantities of material with similar infra-red spectra could be leached from the product with acetone, methanol or water, the bulk of the material is insoluble in all the usual solvents and did not melt below 360 °C. Elemental analyses of samples from different experiments varied somewhat and are in poor agreement with an empirical formula $\text{C}_7\text{H}_5\text{O}_4$ which is suggested by the loss of one molecule of carbon dioxide from five molecules of acid but analysis of highly cross-linked polymers is notoriously difficult. The material swells in dilute sodium hydroxide solution and ion-exchange capacity measurements give a value of 6.4 mequiv./g of dry resin, suggesting that about half the oxygen is present as carboxylic acid groups ($\text{C}_6\text{H}_4\text{O}_2 \cdot \text{CO}_2\text{H} \equiv 6.54$ mequiv./g). Prolonged heating with dilute alkali causes complete dissolution of the resin and acidification and distillation of the concentrated hydrolysate gives an aqueous solution containing acetic and formic acids identified by their retention times on a 'Poropak Q'^a column using flame ionisation and hot wire detectors. The residue from the distillation contained an amorphous acidic material whose infrared spectrum is similar to that of the starting material in showing only broad bands attributable to the carboxyl group. The further examination of this material was hindered by the presence of silicates leached from the walls of the flask during the prolonged hydrolysis.

It has been suggested⁸ that propiolic acid, under conditions of pressure and temperature somewhat different from those reported here, forms a ladder polymer, although the spectroscopic evidence presented is also consistent with a random, rather than a regular, network. The present observations suggest a similar network structure containing cross-linking $(-\text{CO}_2)_2\text{CH} \cdot \text{CH}_2\text{CO}_2\text{H}$ groups, and possibly $-\text{CO}_2\text{CH} = \text{CH} \cdot \text{CO}_2\text{H}$ groups, which arise from the addition of carboxyl groups to the acetylenic bond of propiolic acid. Such groups would be initially hydrolysed to formylacetic acid and then further to formic and acetic acids.

3.7 Other acetylenic monomers

No polymerisation has been observed when 2-butyne-1,4-diol and 1,4-bis (dimethylamino)-2-butyne are heated separately under pressure. Acetylene dicarboxylic acid is unchanged at 23.5 kbar and 100 °C, but at 150 °C is converted to a carbonaceous mass. 3-Bromoprop-1-yne (propargyl bromide) is largely unchanged at 100 °C and 10 kbar, but at 200 °C and 10 kbar and 100 °C at 23.5 kbar, even when diluted with light petroleum, hydrogen bromide and a carbonaceous mass was obtained.

3.8 Methylallene (1,2-butadiene)

This monomer, although not an acetylene, was examined briefly because it is isomeric

^aTrade name of Waters Associates, Inc.

with the butynes and 1,3-butadiene. Preliminary experiments indicate that it polymerizes about as readily as 1-butyne, but the exothermic reaction tends to produce carbonaceous materials. In one experiment a colourless, insoluble polymer was obtained by raising the temperature slowly to 147 °C at 9 kbar. The infrared spectrum of this polymer, which showed strong aliphatic C–H absorptions and weaker absorptions due to C=C bonds, was different from those from the butynes and 1,3-butadiene.

4. Conclusions

Six acetylenic monomers have been polymerised by heating under pressure to either intractable or low melting solids. The polymerisations are highly exothermic and require careful control. Four other monomers failed to polymerise under the conditions examined and although further experiments might produce polymers from these it is unlikely that the physical characteristics of such polymers would be markedly different from those obtained. It seems, therefore, that high pressure reactions are unlikely to provide that route to commercially viable polymers from acetylenic monomers which has so far been lacking.

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