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Polymerization under a Pressure of 6 GPa

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ABSTRACT: Pressures of 6 GPa (ref 52) generated in a tetrahedral anvil pressure apparatus were used for polymerization of addition monomers. With this technique, polymers of moderate and high molecular weight were obtained from selected α-olefins, internal olefins, dienes, and trioxane. The polymers were characterized by their elemental analysis and IR and ^{1}H NMR spectra and have the structure of addition polymers without rearrangements. Success of the polymerization depended on the proper containment of the monomers, which were usually low-boiling liquids; the reaction vessels, specially designed for these pressure experiments, were sealed platinum ampules. The polymerization of a number of monomers which had not been polymerized before has been achieved. It depended on the favorable dependence of the rate of propagation over the rate of termination or transfer. The polymerization reaction mechanism appears to be a thermally initiated radical process with the possible exception of trioxane.

High pressure has been used to carry out reactions not possible at atmospheric pressure and to accelerate the rate of other reactions.[1,2] Rates of reaction in the condensed phase are accelerated under high pressure and many chemical equilibria depend very much on pressure.[3] The effect of pressure on kinetics varies, but rate constants in favorable cases can increase by several orders of magnitude. This acceleration is usually attributed to effects on the volume of the transition state and in rare cases inverse effects have been found.

Several pressure ranges have been studied for pressure reactions which are determined by the availability of pressure vessels and devices to produce the corresponding pressures and for the specific reactions which are desired to be performed. The lower pressure range is the range below 100 MPa; a second pressure range is between 100 MPa and 1 GPa and a number of chemical processes, especially gas phase reactions, are carried out in the pressure range up to 400 MPa. A third range consists of pressures of more than 2 GPa.

In the fifties pressure apparatus was developed based on Bridgman's "principle of massive support" and solid pressure transmitters and possessing useful working volume. This made synthesis research practical at pressures of more than 5 GPa and temperatures up to 1500 °C. A most convenient device for this work is the tetrahedral anvil apparatus, developed by Hall[4-6] and modifield at the National Bureau of Standards. The early studies were limited to solids because no container was known which could contain liquids in the tetrahedral anvil apparatus. Recent development[8-12] of a device to contain liquids with boiling points as low as −10 °C has allowed study of the polymerization of liquids under these heroic conditions. A preliminary account was published some time ago.[8]

Most studies of polymerization under pressure have been made in the pressure range up to 1.2 GPa. It has been found that the ceiling temperature of polymerization was greatly affected by increases in pressure; for example, it was shown that the ceiling temperature of α-methylstyrene was increased from 61 °C at 0.1 MPa to 170 °C at 650 MPa. It is therefore not surprising that a number of polymers with ceiling temperatures much below room temperature, for example, polymers of aliphatic aldehydes, have been first prepared under pressures of about 1 GPa.[13]

Perhaps the most important commercial polymer prepared under pressure is polyethylene where pressures up to 400 MPa are used. This polymer has a branched structure as prepared under these conditions; however, if the pressure is increased to 1 GPa an essentially linear polymer of polyethylene is obtained.[14-18] Other compounds which cannot be polymerized under normal conditions are perfluorinated α-olefins notably hexafluoropropylene.[19] Other perfluoro-α-olefins with long side chains polymerize only under pressures of up to 2 GPa.[20] 1,1-Disubstituted ethylenes, such as α-methylstyrene,[21] polymerize even to higher molecular weight under high pressure.

Attempts made to polymerize *trans*-stilbene at 90 °C and 500 MPa were unsuccessful.[22] However, it is known that stilbene, 2-butene, and cyclopentene copolymerize readily with ethylene even at normal pressures but require coordination catalysts.[23] 1,2-Disubstituted ethylenes have not been homopolymerized to high molecular weight polymers even under elevated pressures.[24,25] Some functionally substituted 1,2-disubstituted olefins, containing a carboxylate group, have however been polymerized and it has been found that they polymerize under higher pressure[22,26,27] to higher molecular weight.

Tri- and tetrasubstituted ethylenes have also been subjected to high pressures in attempts to obtain polymers. A very small yield of dimer was obtained from α,β-dimethylstyrene at 500 MPa and 120 °C. Trimethylethylene

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at 270 °C and 300 MPa gave a good yield of products, mostly dimers. Tetramethylethylene at nearly 300 °C and pressures up to 2.75 GPa gave reasonable conversions to tetramers and pentamers but the structures of these materials were not shown to be linear polymers.[28–30]

Most polymerization reactions that have been studied at higher pressures are radical reactions although ring-opening polymerizations of cyclic ethers were done also in the presence of ionic initiators.[31,32]

The net effect of pressure on polymerization of a compound clearly depends on the influence of pressure on the individual rate constants of initiation, propagation, and termination. These rates were studied very carefully in the polymerization of styrene[33] (eq 1). The acceleration

$$\frac{\delta \ln k}{\delta P} = \frac{-\Delta V^{\ddagger}}{RT} \qquad (1)$$

k = rate of reaction; P = pressure; $\Delta V^{\ddagger}$ = volume change of transition state; R = gas constant; T = temperature

of the polymerization by pressure is caused by the increase of the rate of chain propagation and a decrease in the rate of termination of the kinetic chain.[8] It is reasonable to believe that the propagation step shows a larger decrease in transition state volume and thus a larger rate increase than does the termination reaction which requires the diffusion of two polymeric and relatively nonmobile radicals to find each other. The initiation rate constant is believed to be negatively influenced because radicals are normally prepared by dissociation of a neutral molecule and this dissociation is most likely to be prevented from occurring under conditions of high pressure. At relatively high temperatures, which are sometimes necessary to maintain the mobility of the monomer, chain-transfer reactions are predominant and cause the formation of low molecular weight material.

Polymers of substituted ethylenes can exist in structures of different stereoregularity. As high-pressure polymerizations proceed in the condensed phase, it is possible that the polymer with the smallest volume might be formed preferentially. It has, however, been found that this influence is not very important. The polymerization of methyl methacrylate under pressure was studied but only a slight increase in the percentage of isotactic triads was noticed when the polymerization was carried out at 0.1 MPa or at 800 MPa pressure.[34,35]

Experimental Section

Materials: Cyclopentene (Aldrich Chem. Co., purissima), cyclohexene (Phillips Petroleum Co.), cycloheptene (Aldrich Chem. Co., tech., 95%), cyclooctene (Aldrich Chem. Co., 95%), cyclododecene (Aldrich Chem. Co., tech.), 1-methylcyclopentene-1 (Aldrich Chem. Co., 96%), 1-methylcyclohexene-1 (Phillips Petroleum Co.), 3-methylcyclohexene-1 (Aldrich Chem. Co., 98%), 4-methylcyclohexene-1 (Phillips, 95% redistilled), 1-phenylcyclohexene-1 (Aldrich Chem. Co., 99%), methylenecyclohexene (Eastman Kodak Co.), 1-methylcycloheptene-1 (research sample), 3-methylcyclooctene-1 (research sample), norbornene (Aldrich Chem. Co., 99%), cyclohexadiene-1,4 (Aldrich Chem. Co., 97%), cyclohexadiene-1,3 (Aldrich Chem. Co., 99%), norbornadiene (Aldrich Chem. Co., 99%), cyclooctadiene-1,5 (Phillips Petroleum Co.), cyclododecatriene (trans, trans, cis) (Aldrich Chem. Co.), 1-methylcyclohexadiene-1,4 (research sample), butene-1 (Phillips Petroleum Co.), pentene-1 (Phillips Petroleum Co.), isobutylene (Phillips Petroleum Co.), hexene-1 (Phillips Chemical Co.), 3-methylpentene-1 (Aldrich Chem. Co., 99%), styrene (Aldrich Chem. Co., 99%), α-methylstyrene (Aldrich Chem. Co., 99%), *cis*-butene-2 (Phillips Petroleum Co., 99% pure), *trans*-butene-2 (Phillips Petroleum Co., 99.8% pure), *cis*-pentene-2 (Phillips Petroleum Co., reagent grade), *trans*-pentene-2 (Farchan Research Labs., >99%), hexene-2 (Phillips, pure, used as obtained, 85% cis and 15% trans as judged by infrared analysis), 2-methylbutene-2 (Phillips Petroleum Co.), 2,3-dimethylbutene-2 (Aldrich Chem. Co., 99+ %), butadiene-1,3 (Phillips Petroleum Co.), 2-methylbutadiene-1,3 (Eastman Kodak Co.), 2,3-dimethylbutadiene-1,3 (Eastman Kodak Co.), 1-methylbutadiene-1,3 (cis/trans mixture) (Phillips Petroleum Co.), 2-chlorobutadiene-1,3 (DuPont Co.), 2,3-dichlorobutadiene-1,3 (DuPont Co., research sample), 2-cyanobutadiene-1,3 (DuPont Co., research sample), 1-cyanobicyclo[3.1.0]hexane (Dupont Co., research sample), and trioxane (Celanese Chem. Co.).

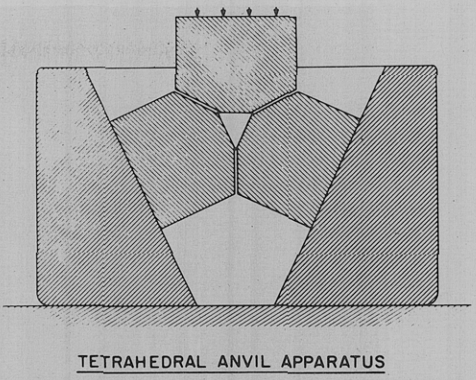


Figure 1. Sketches of the principles of the tetrahedral anvil apparatus.

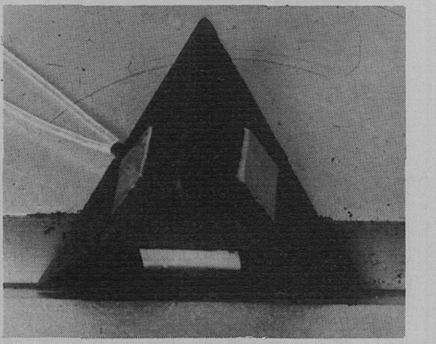


Figure 2. Photograph of the tetrahedral part.

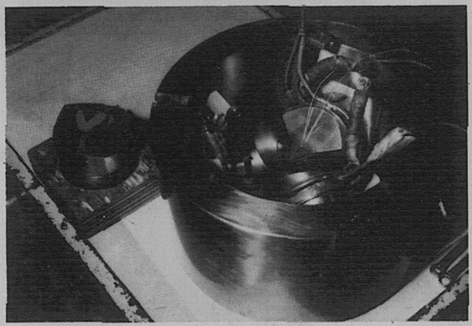


Figure 3. Photograph of the central part of the tetrahedral anvil high-pressure apparatus.

In general, the compounds were purified by passing them over alumina to remove peroxides and to dry them over molecular sieves 5A. They were transferred using vacuum technique.

cis-Pentene-2 was purified by gas chromatography and contained 99.1% cis isomer.

Measurements. Infrared spectra were recorded on a Perkin-Elmer 21 infrared spectrometer. Proton magnetic spectra ^{1}H-NMR were obtained on a Varian 60 MHz spectrometer or on a Varian 220 MHz spectrometer.

High-pressure reactions were carried out on a tetrahedral anvil or on a Bridgeman-Monoblock apparatus. The details are described below (Figures 1–3).

Procedures. The problem of studying the effect of pressure on liquids above 2.5 GPa has been one of preparing a suitable container for use in the tetrahedral anvil apparatus. In the 1-in. device the space for the reaction vessel is 9.6 mm long and 6.0 mm in diameter. Platinum ampules have been devised to fit this cavity.[9] The ampule was constructed by soldering the ends and

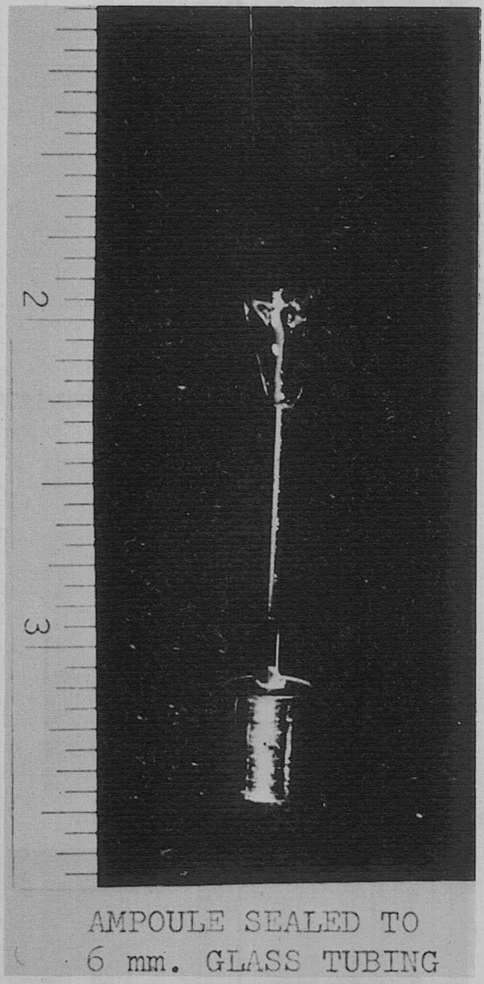


Figure 4. Platinum ampule for high-pressure reactions.

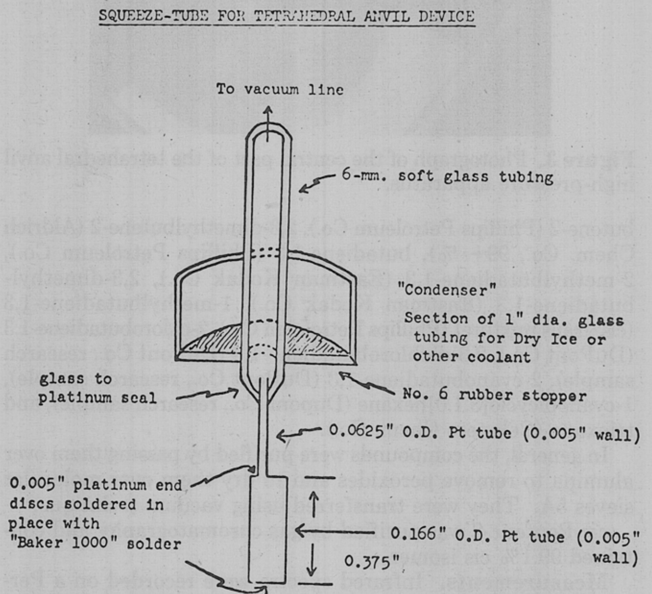


Figure 5. Sketch of the filling procedure of platinum ampule.

the filler tube to the body of the ampule with "Baker 1000" solder (a proprietary alloy of Pd, Au, and Ag of undiclosed composition),[9] melting at 1000 °C. The neck of the ampule was sealed into a 6 mm soft glass tube about 100 mm long. The glass to platinum seal could be immersed in dry ice or liquid nitrogen and remained vacuum tight (Figure 4). A short jacket was filled with liquid nitrogen and the liquids distilled (or syringed) into the cold portion of the glass tube (Figure 5). When the system had been degassed, the platinum part was cooled with liquid nitrogen and the liquid in the tube was allowed to run into the ampule. After appropriate precautions had been taken to insure that the tube was not over-full, the neck was flattened and clamped in a vise with jaws 1.6-mm thick and tightened with a torque wrench at a torque of 5 pounds to seal it. The neck was then cut above the seal and welded with a gas oxygen torch. While the ampule was cooled (Figure 5), there may have been a small amount of air introduced into the sample which was held between the seal and the weld (Figure 6A). With proper technique it is unlikely that any air entered the neck because it was crimped tight and held in the vise and the shearing actions of the scissors or pliers would tend to seal the platinum tube. An occasional introduction of oxygen cannot be entirely excluded. Amounts between 60 and 200 mg (depending on the density of the liquid) could be sealed in these ampules and materials boiling as low as −10 °C (isobutylene) could be handled by this technique. When attempts were made to fill ampules with liquids boiling below −10 °C, the ampules bulged when they were warmed to room temperature. The neck was bent 90° and encased in compacted zinc powder. The ampules were inserted into the sample cavity in the pyrophyllite tetrahedron. Alternating current for heating was passed through the cylindrical wall of the ampule. This geometry minimizes the temperature gradient between the center and the ends of the ampule in the tetrahedral anvil device and we believe the pressure is relatively constant throughout the sample. As will be mentioned later, some variability from run to run was experienced. After a reaction period of 3 to 6 h at 6 GPa and temperatures up to 300 °C, the ampules have a characteristic flattened shape (Figure 6B). The ampules were weighed and cut open with a razor blade, the contents qualitatively observed (Figure 7A,B), and the ampule and its content placed in a vacuum apparatus of 10^{-3} Pa for 2 to 16 h.

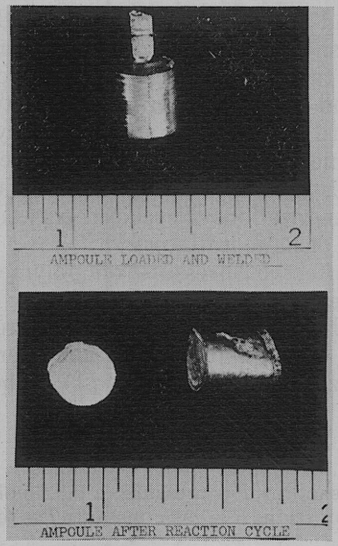


Figure 6. Platinum ampule: (a) sealed and ready for pressure reaction; (b) after reaction.

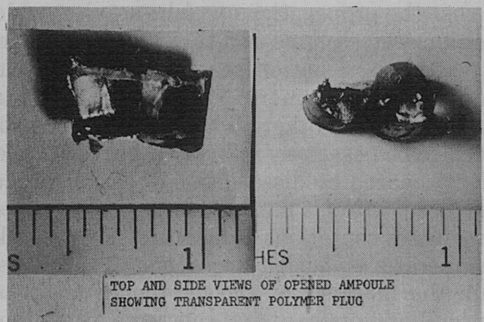


Figure 7. Opened platinum ampule after reaction.

The products were dissolved in a solvent or in some cases removed directly from the ampule if solid. The open part of the ampule was cleaned, dried, and reweighed, allowing calculation of the yield. Successful polymerization reactions of most olefins yielded viscous oil and waxy solids. In a few cases, hard solid polymers were obtained.

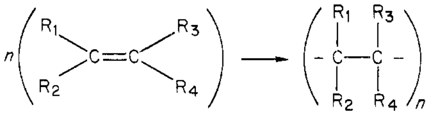
Because there were many possibilities of leaks and mishaps both during the filling operations of the sample ampules and the actual pressure reaction, initially very few successful runs were recorded, but with experience a point was reached where 80% of the runs were successful which means they gave products without leaks or other failures. However, run to run variations in product yield and molecular weight were very substantial; for example, when a number of polymerizations of cyclopentene were carried out in order to obtain a sufficient amount of material for characterization, the products ranged from thick oils to waxy solids without it being possible to identify clearly the reasons for the run to run variations.

Because of the small amount of material normally obtained (100 mg) from each run in the tetrahedral anvil apparatus, only limited polymer characterization could be carried out. Of primary importance was the elemental analysis, the determination of the infrared spectrum, and, when possible, the ^{1}H NMR spectrum of the individual polymers. On some examples the inherent viscosity was also measured, but viscosities, in general, were below 0.1 dL/g. Polycyclopentene was also subjected to DTG, DSC, and mass spectral analysis which showed masses of up to 1200 mass numbers but only part of the sample volatilized.

Reactions in the Bridgeman-Monoblock were carried out at pressures from 10 to 25 GPa at 300 °C, the sample being contained in a Teflon cup. In the Monobloc apparatus, a plot of distance traveled vs. temperature can show the temperature at which contractions or expansions other than those during the heating occur. It was found that polymerization occurred between 280 and 300 °C. Since it appeared likely that the polymerization occurred in the solid phase (no break in the displacement vs. temperature curve to indicate melting), it was felt that increased mobility in the sample might be necessary for a successful polymerization. However, in an experiment where $^1/_3$ of the charge was petroleum ether, no polymerization occurred in the Monoblock whereas when the charge was the neat monomer polymerization occurred smoothly.

Results and Discussion

Nearly 50 monomers, olefins, dienes, and miscellaneous monomers, many of which have not been polymerized before, were subjected to up to 6 GPa of pressure in the tetrahedral anvil at temperatures of up to 300 °C and most compounds produced polymers under these reaction conditions (eq 2). The polymers were viscous oils to waxy greases and in some cases hard solids. Because of the small amount of materials, only limited characterizations could be carried out; characterization was impeded because of run to run variations which precluded combining samples.



$$n\left(R_1R_2C{=}CR_3R_4\right) \longrightarrow \left(-\overset{R_1}{\underset{R_2}{C}}-\overset{R_3}{\underset{R_4}{C}}-\right)_n \qquad (2)$$

The polymers were characterized primarily by elemental and infrared analyses. In some cases, ^{1}H NMR analysis was used although sample size was a problem. It was demonstrated that bond opening had occurred by 1,2 addition without any noticeable rearrangement. In applicable cases, samples were carefully compared with polymers obtained by other routes from the same monomers.

Although in many cases the polymers were very viscous liquids, they were shown to have a degree of polymerization of at least 10. End groups were not identifiable by IR analysis although the spectra of thicker sections of the polymers showed some olefinic absorption at 6.1 μm presumed to be end groups. Small peaks in certain specific cases in the fingerprint region beyond 10 μm indicated unsaturation caused by terminal double bonds. Absorption at 5.85 μm in some samples may indicate the presence of carbonyl groups, perhaps introduced from the small amount of oxygen which was present in the small section of the vial after sealing.

No initiator was normally used for the high-pressure polymerizations. Experiments with added initiators did not differ from controls and of course the decomposition temperature of peroxides and azonitriles (used as initiators) at 6 GPa is unknown. It is believed that the polymerizations were either initiated thermally or by a small impurity of oxygen. However, the possibility of the platinum surface acting as initiator cannot be excluded.

Nothing is known about the state of the monomer at these pressures during the polymerization. There is no doubt that all monomers are in the solid state at full pressure during the reaction and high temperatures were necessary to introduce some mobility into the monomer matrix allowing polymerization to occur. Below 200 °C no polymers were obtained even at 6 GPa. For example, in the case of cyclopentene, a reproducibly polymerizable monomer under these conditions, a very low yield of low molecular weight material was obtained at 200 °C and more at 250 °C, but good results were only obtained at 300 and 350 °C. Much above these temperatures, side reactions seemed to take place and low yields of polymer were obtained or the sample tubes ruptured. Even though the exact state of the monomer during the polymerization reaction is unknown, it is believed to be in the glassy, crystalline or partially crystalline state. Variations in the physical state of the monomers might explain why the reproducibility of these polymerization runs is poor. The exact state of the monomer could depend on the way the pressure is applied, rate and change of nucleation, if any, state of purity of the monomer, or even the heating rate. Hydraulic pressure (3500 psi) is applied to a 16 in. diameter ram in a 500-ton hydraulic press, which in turn pushes on the 4.5 in. diameter back of each of four anvils. Thus the 3500 psi pressure is multiplied by $16^2/4.5^2$ at the *backs* of the anvils of the tetrahedral anvil apparatus and the multiplied pressure is transmitted through soft stone to the meal container (Figures 1 and 2) to give a pressure on the surface of the reaction ampule of 6 GPa. In cases where some solid polymer was obtained at the end of the polymerization, it could be seen that the solid was at the walls of the platinum container which might mean that either the pressure applied was higher near the surface of the container which is less likely or that the temperature was higher at the surface which is very likely causing higher mobility for this polymerization. Such cases indicate an effective application but relatively poor uniformity of temperature and pressure on the platinum ampules in these high-pressure experiments.

Melting points of organic compounds often follow the expression $T^c/T_0 = [P(\text{atm}) + a]/a$. For benzene, *over the range studied*, $a = 3775$ and $c = 2.49$. The calculated melting points are 311 °C at 2 GPa and 617 °C at 6 GPa. The melting point of α-methylstyrene has been measured and was found to be −24 °C at 1 atm, at 380 MPa it is 61 °C, and at 1 GPa it is 200 °C. Linear extrapolation of 2.2 °C/10 MPa melting point elevations would amount to a melting point for α-methylstyrene at 6.5 GPa of 1400 °C.

The ceiling temperature of α-methylstyrene also goes up from 61 °C at 0.1 MPa to 170 °C at 650 MPa or 1.7 °C/10 MPa ceiling temperature elevations. It is most likely that neither melting point nor ceiling temperature increase linearly with pressure at higher pressures, but even at an average of 1 °C per 10 MPa, pressure increase would give an increase of the melting or ceiling temperature of

600 °C for a pressure increase to 6 GPa.

If we do not consider the freezing point of the monomers but rather the point of mobility, an estimate can be made from known polymerizations in the solid and glassy state where some mobility is necessary for the polymerization to proceed. The temperature of mobility as determined by dielectric measurements and solid-state NMR measurements of low molecular weight compounds is about 30–50 °C below the actual melting point. This influence is small compared to the enormous increase of the freezing temperature and suggests that even if the monomers remain in the glassy state after the application of the pressure, temperatures of 300 °C are necessary to induce sufficient mobility in the sample for polymerization to occur.

Occasionally temperature increases in the monomer samples have been noted at the moment high pressure is actually applied to a sample. In this work, it was only possible to measure the temperature on the surface of the reaction vessel and the temperature in the center of the sample could be slightly different. In most experiments, local temperature increases during the application of the pressure were not observed. In any case, recovery of unreacted materials from lower temperature runs seems to ensure that local heating during compression is not significant.

On some occasions, exceptions to the temperature requirements of 300 °C for a successful reaction were observed as reactions other than polymerization reactions took place in an apparently explosive manner. In the case of some dienes and epoxides as well as with acrylonitrile, explosive reactions were observed even at temperatures as low as 150 °C, and a rapid temperature rise to 500 and even 1000 °C was registered. The reaction product in those cases was not the expected polymer but a black powder of high carbon content.

Substantial work was done in the study of the polymerization of cyclopentene which will consequently be treated first and separately.

Polymerization of Cyclopentene. Cyclopentene was polymerized in the tetrahedral anvil apparatus at 6 GPa and 300 °C for 6 h. In an average of several runs a 75% yield of polycyclopentene was obtained; in the best cases, a waxy material which showed a molecular weight by mass spectroscopy of greater than 1200 was obtained. Fractionation yielded 12% solid material and 88% of very viscous oil. The oil had an inherent viscosity of 0.05–0.1 dL/g and a polydispersity (M_w/M_n) measured by GPC in a 5% solution in cresol of 2.2. The solid polymer had a transition region of 60–70 °C. Programmed thermal degradation of this polycyclopentene at 6 °C per min, under nitrogen, showed a weight loss of 12% at 275 °C and a maximum rate of degradation near 475 °C. The polymer degradation did not begin at a substantial rate until the temperature was above 350 °C, but the degradation showed a broader degradation spectrum than is normally noticed with other degradation spectra of polymers. The maximum rate of polymer degradation of polycyclopentene prepared by high-pressure polymerization is at a temperature just below that of polypropylene, suggesting that the structure of polycyclopentene is relatively unstrained.

The conditions for the polymerization of cyclopentene were varied in order to determine the optimum conditions for this and for other high-pressure polymerizations. In 3 h, at 6 GPa at a reaction temperature of 350 °C, a clear, brittle polymer was obtained while at a temperature of 200 °C only a viscous oil was isolated. At reaction temperatures below 200 °C there was no polymerization at 6 GPa.

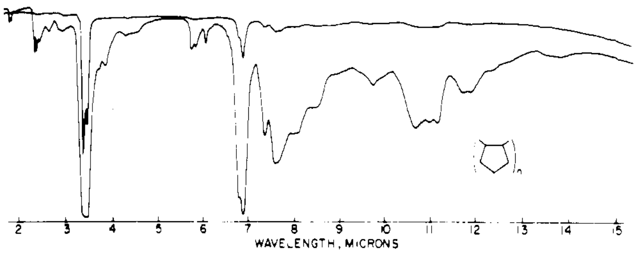


Figure 8. IR spectrum of polycyclopentene.

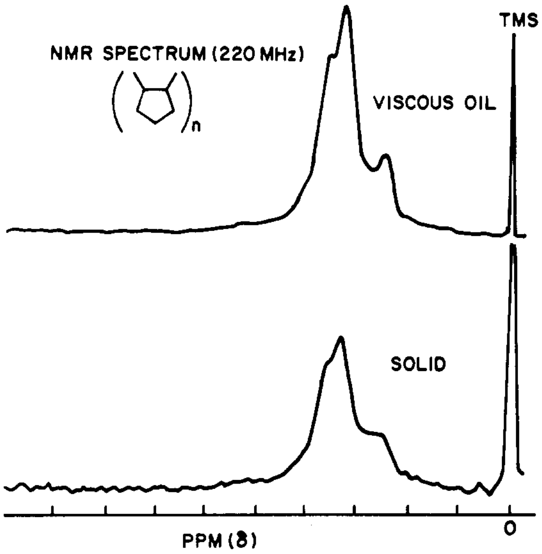


Figure 9. ^{1}H NMR spectrum of polycyclopentene.

When the polymerization was carried out in the Bridgeman-Monobloc at 300 °C in 4 h at 2.2 GPa, a viscous oil was obtained. From the sample of volume damage in the reactor, it was noticed that the polymerization apparently began at 280 °C. No polymerization occurred when the cyclopentene was subjected in the Bridgeman apparatus to 300 °C for 6 h and 10 GPa.

The infrared spectrum of a polycyclopentene sample of about 0.01 mm thickness between sodium chloride plates showed absorptions at 3.36 μm with a second smaller peak at 3.41 μm. A somewhat smaller absorption peak was found at 6.87 μm with a shoulder at 6.76 μm. If the IR spectrum of samples of 0.1 to 0.2 mm were taken, additional absorption peaks were observed at 3.85 μm and at 7.35 μm followed by broad peaks of decreasing intensity at 7.6, 8.0, and 8.5 μm. There is an additional peak at 9.75 μm and broad absorptions in the 10.7–11.2 and 11.7–1.9-μm region. Other absorption peaks at 6.05 μm showed the apparent residual unsaturation and a double peak at 5.75 and 5.85 μm was caused probably by a trace carbonyl impurity (Figure 8).

The 60 MHz ^{1}H NMR spectrum of polycyclopentene in chloroform showed a broadened resonance at τ 8.5 with a somewhat separated peak at the higher field part of the spectrum and a shoulder at the lower field part. No better resolution was obtained when the spectrum was run at 220 MHz. It is probable that the higher field peaks were caused by the methine protons, the central peak by the protons of the methylene group near the chain, and the lower field two methylene protons were those which are farthest from the polymer backbone chain (Figure 9).

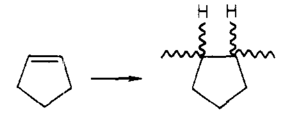
The absence of any substantial amount of double bonds in the infrared spectrum and also the absence of any double bond in the ^{1}H NMR spectrum (the area ratio of the region δ 0–4 over δ 4–8 was 80:1) indicates that the structure of the high-pressure polymer of cyclopentene is

Table I
Polymerization of Unsubstituted Cyclic Olefins[a]

			anal.				
			calcd		found		
cyclic olefins	yield, %	remarks	C	H	C	H	
cyclopentene	75	solid	88.16	11.84	88.04	11.95	$(C_5H_8)_n$
cyclohexene	80	solid	87.73	12.27	87.56	12.43	$(C_6H_{10})_n$
cycloheptene	65	brittle solid	87.42	12.58	87.69	12.30	$(C_7H_{12})_n$
cyclooctene	60	clear grease	87.19	12.81	87.17	12.82	$(C_8H_{14})_n$
cyclododecene	55	viscous polymer	86.66	13.34	86.57	13.42	$(C_{12}H_{22})_n$

[a] Pressure 6 GPa, time 4 h, temperature 300 °C.

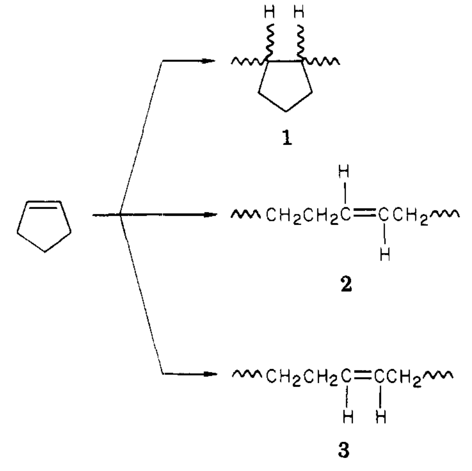
a polycyclopentene which is obtained by 1,2 polymerization as seen in eq 3 and no other partial structure need be considered.



(3)

Cyclopentene has been polymerized in the past by coordination polymerization; with tungsten and molybdenum catalysts, cis and trans pentenamers have been obtained.[36-38] These polymers are clearly different from our high-pressure polycyclopentene as they have open chain structure without cyclopentane rings and have characteristic cis or trans double bonds which can be seen in the infrared spectrum. The typical specific double bond absorption of the cis polypentenamer is at 14 μm (Figure 10A) and that of the trans polypentenamer near 10 μm (Figure 10B), regions which are completely free of absorption in our polycyclopentene.

Cyclopentene has also been polymerized with titanium containing coordination catalysts. A polymer which consists of cis and trans pentenamer units as well as with unchanged cyclopentane units in the polymer chain[38] was obtained (Figure 10C) (eq 4). Comparison of spectra in Figure 8 with Figure 9 and analysis of the ^{1}H NMR spectra clearly indicates that our polycyclopentene is obtained by 1,2 bond opening polymerization and no ring opening (metathesis) had occurred.



(4)

Since the high-pressure polymerization occurs in the absence of metal catalysts, it is probably a thermal, free-radical reaction and it is not surprising that ring-opened structures are not found in the polymer structures. While the reaction ampule was made of metallic platinum, there is no precedent that the metathesis reaction needed to open the cyclopentene ring was operative under these conditions.

Polymerization of Other Cyclic Olefins. Polycyclohexene. Polymerization of cyclohexene in the tetrahedral anvil apparatus gave an 80% yield (Table I) of polycyclohexene as a white solid product or a waxy polymer of an inherent viscosity of 0.03 dL/g. At pressures as low as 3 GPa a white solid product could be isolated if the reaction was carried out at 300 °C for 6 h. Under otherwise identical conditions but at 200 °C the reaction gave a product which was a sticky oil. When the reaction was carried out under the same pressure for half an hour at 500 °C, carbonization occurred. In the Bridgeman-Monoblock at 300 °C at 2.2 GPa for 4 h, cyclohexene was transformed into a viscous oil. It was noticed that the polymerization seemed to occur at 300 °C (a slight decrease of volume was observed in the pressure record).

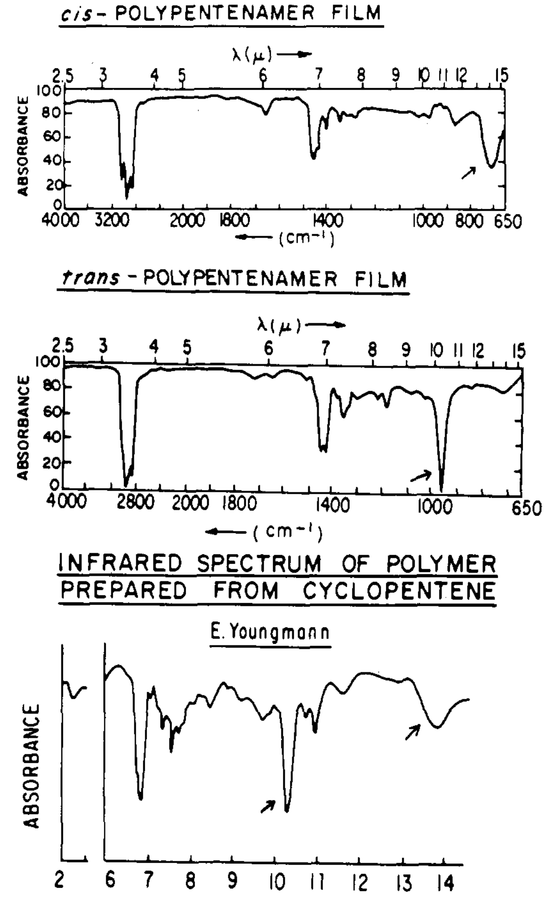


Figure 10. IR spectra of (a) *cis*-pentenamer; (b) *trans*-pentenamer; (c) and Youngmann's polymer

Several attempts were made to improve this polymerization of cyclohexene using initiators and diluents. No effect was found by adding benzoyl peroxide as the initiator and the same polymer in similar yield was obtained. Because of the experimental setup we could not be sure the benzoyl peroxide had undergone the expected decomposition and produced the initiator fragments, the

Table II
Polymerization of Substituted Cyclic Olefins[b]

		anal.				
		calcd		found		
cyclic olefins	yield, %	C	H	C	H	
1-methylcyclopentene	90	87.73	12.27	87.93	12.07	$(C_6H_{10})_n$
1-methylcyclohexene	80	87.42	12.58	87.44	12.55	$(C_7H_{10})_n$
3-methylcyclohexene	70	87.42	12.58	87.57	12.24	$(C_7H_{10})_n$
4-methylcyclohexene	90	87.42	12.58	87.19	12.80	$(C_7H_{10})_n$
1-phenylcyclohexene	*a*					$(C_{12}H_{14})_n$
methylenecyclohexane	*a*					$(C_7H_{12})_n$
1-methylcycloheptene	92	87.19	12.81	87.23	12.81	$(C_8H_{14})_n$
3-methylcyclooctene	90	87.02	12.98	87.07	12.92	$(C_9H_{16})_n$
norbornene	*a*	89.29	10.71	89.15	10.85	$(C_7H_{10})_n$

[a] Yield was not determined. [b] Pressure 6 GPa, time 4 h, temperature 300 °C.

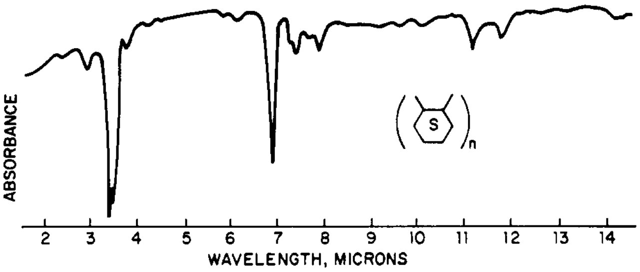


Figure 11. IR spectrum of polycyclohexene.

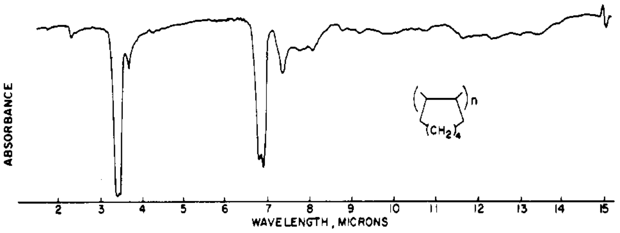


Figure 12. IR spectrum of polycyclooctene.

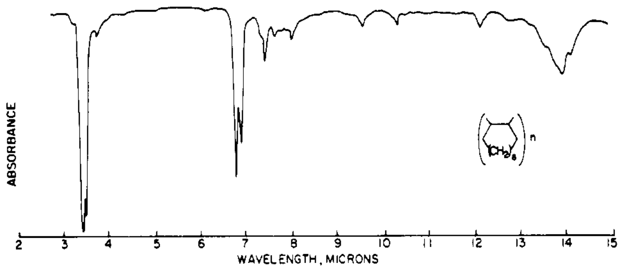


Figure 13. IR spectrum of polycyclododecene.

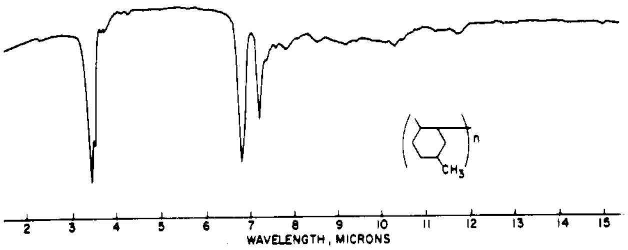


Figure 14. IR spectrum of poly(4-methylcyclohexene).

phenyl and benzoyl radicals. When isopentane was added to the cyclohexene, no polymerization occurred. It had been expected that isopentane would provide additional mobility in the matrix and consequently facilitate the polymerization of cyclohexene under extreme measures. In retrospect, it might be argued that one should have expected a negative effect of dilution if both monomer and diluent were in the same phase; the effect might be explained by saying that the monomer molecules in dilution cannot be forced into the close proximity in the transition state necessary for a successful polymerization, a situation which exists with bulk monomer polymerization.

The infrared spectrum of the polycyclohexene showed strong bands at 3.4 and 3.5 μm with a smaller absorption peak at 3.75 μm in thicker samples. An additional strong peak is at 5.94 μm and smaller peaks at 7.4 and 7.9 μm as well as at 11.4 and 11.8 μm; a very small peak could be seen at 7.6 μm in thicker samples (Figure 11). The ^1H NMR specturm showed a large, complex peak at δ 1.4 but the integration showed an 80:1 ratio of the aliphatic protons over vinylic protons. Since termination may be by recombination and not by disproportionation, this ratio cannot be used for the estimation of molecular weight.

Cycloheptene. Polycycloheptene was also obtained by polymerization at 6 GPa and 300 °C for 4 h (Table I).

Cyclooctene. Under polymerization conditions similar to those described for cyclopentene and cyclohexene, cyclooctene was polymerized to polycyclooctene in good yield (Table I). A type of polymerization of cyclooctene has been accomplished with transition metals, coordination catalysts,[39] or free-radical initiators.[40] The structure of the product, however, has not been unequivocally proven. The infrared spectrum of our polycyclooctene showed strong bands at 3.4 and 3.5 μm with an additional small peak at 3.75 μm. A strong double absorption peak at 6.8 and 6.9 μm and a somewhat weaker peak at 7.3 μm was followed by even smaller ones at 7.9 and 8.1 μm. There are smaller peaks throughout the spectral region up to 14 μm (Figure 12) when very thick samples of polycyclooctene are studied.

Cyclododecene. Cyclododecene polymerized at 6 GPa in 3 h at 300 °C. A liquid viscous polymer obtained from which fibers could be drawn (Table I). The infrared spectrum of the polymer is shown in Figure 13; it shows strong bands at 3.4 and 3.5 μm with a small absorption peak at 3.75 μm. Strong peaks are also observed at 6.8 and 6.9 μm. The intensity of these peaks, however, is reversed as compared to those of polycyclooctene. There are additional smaller but not significant peaks at 7.45, 8.0, 9.6, 10.4, and 12.2 μm and a strong broad absorption is found at 14.0 μm (Figure 13).

Polymerization of Substituted Cyclic Olefins. Cyclic olefins with five-to-eight-member rings substituted with methyl groups were also successfully polymerized at 300 °C and 6 GPa in the tetrahedral anvil apparatus to viscous oils and greases.

1-Methylcyclopentene. 1-Methylcyclopentene was polymerized in 90% yield to the corresponding polymer (Table II).

4-Methylcyclohexene. The polymer of this compound was obtained in 80% yield. The infrared spectrum of the liquid polymer (Figure 14) indicated strong bands at 3.4

Table III
Polymerization of Cyclic Dienes[b]

		anal.				
		calcd		found		
cyclic dienes	yield, %	C	H	C	H	
1,4-cyclohexadiene	98	89.94	10.06	89.58	10.31	$(C_6H_8)_n$
1,3-cyclohexadiene	97	89.94	10.06	89.12	10.87	$(C_6H_8)_n$
norbornadiene	*a*	91.25	8.75	91.14	8.85	$(C_7H_8)_n$
1,5-cyclooctadiene	*a*	88.82	11.18	88.83	11.16	$(C_8H_{12})_n$
trans,trans,cis-cyclododecatriene	90	88.82	11.18	88.63	11.37	$(C_{12}H_{18})_n$
1-methyl-1,4-cyclohexadiene	93	89.29	10.71	89.05	10.94	$(C_7H_{10})_n$

[a] Yield was not determined. [b] Pressure 6 GPa, time 4 h, temperature 300 °C.

and 3.5 μm and bands of similar intensity at 6.85 and 7.25 μm; the latter is representative for the methyl group of the cyclohexene ring. There were also small bands at 6.1 (residual double bond) and 5.85 μm (carbonyl stretch), indicating a low molecular weight of this polymer. Very small bands were also noticed at 10.3 and 11.8 μm. A polymer of 3-methylcyclohexene had also been prepared earlier[38] by a different method and showed identifiable small bands at 10.3 and 11.7 μm in addition to the strong carbon–hydrogen bands.

Polymers were also obtained in good yield by high-pressure polymerization from 3-methylcyclohexene, 4-methylcyclohexene, 1-phenylcyclohexene, and methylenecyclohexane (Table II).

1-Methylcycloheptene. This polymer which was obtained in 92% yield (Table II) showed the following infrared spectrum: Strong bands at 3.4 and 3.5 μm with a small one at 3.75 μm, a barely split doublet at 6.85 and 6.95 μm, and a strong indication of the methyl group at 7.3 μm. Smaller peaks are also noticed at 10.2, 10.7, and 12 μm.

3-Methylcyclooctene. A polymer of 3-methylcyclooctene was obtained in 90% yield (Table II) with an infrared band at 3.4 and 3.5 μm with a shoulder at 3.35 μm and a smaller peak at 3.75 μm; there is some indication of a double bond at 6.1 μm. Strong bands were also found at 6.85 μm with a shoulder at 6.9 μm and the methyl group at 7.25 μm with a shoulder at 7.35 μm.

All the polymers described in this section were from substituted cycloolefins and can exist as normal head-to-tail polymers obtained by 1,2 bond-opening polymerization or the polymer structures may contain head-to-head linkages. We have no way of distinguishing between H–H and H–T placements.

Norbornene. Bicyclo[2.2.1]heptene was also polymerized by high-pressure polymerization, by 1,2 polymerization. A polymer of this structure had also been prepared previously[49] by coordination polymerization.

Polymerization of Cyclic Dienes. Cyclic dienes and trienes were polymerized by subjecting them with 6 GPa for 4 h at 300 °C. Polymerizations of cyclic dienes have been studied in the past in the polymerization of cyclohexadiene-1,3, cyclohexadiene-1,4, and cyclooctadiene-1,5, primarily by coordination catalysts.[42] Various polymer structures may be formed during the polymerization of the cyclic dienes. One possibility is the result of the regular 1,2 polymerization with the second double bond left unreacted; 1,4 polymerization, typical for conjugated dienes, can also occur alternatively or rearrangement of the cyclic diene double bonds to a conjugated diene[1,3] can occur followed by polymerization, which would give cyclic structure and a double bond as part of the polymer chain. Another possible polymerization pathway of cyclic dienes includes transanular polymerization. This polymerization will give structures with no double bond in the polymer. The formation of structures by transanular reactions has been suggested for the copolymerization of SO_2 with cyclooctadiene-1,5.[43]

Although polymers of cyclic dienes have been obtained by our high-pressure polymerization techniques, a detailed study of the structure of these polymers has not been made but only the infrared spectra of the polymers have been recorded.

Cyclohexadiene-1,4 was polymerized in 98% yield under our standard high-pressure polymerization conditions. The polymer has infrared bands at 3.40 and 3.5 μm with a shoulder at 3.3 μm and a small band at 3.75 μm. A broad, but significant, band was found centered at 6.05 μm which is indicative for unsaturation. A very complicated and broad band was also found at 6.9 μm with shoulders at 6.8 and 6.7 μm. There is an additional double band near 15 μm and a very small absorption band at 9.8 μm.

The polymer obtained in 97% yield from cyclohexadiene-1,3 (Table III) showed strong bands at 3.4 and 3.5 μm with a well-separated shoulder at 3.3 μm and a small peak at 3.75 μm. A significant doublet was also found at 6.0 and 6.1 μm indicating that the polymer is unsaturated. A strong band at 6.9 μm with shoulders at 6.8 and 6.7 μm was also observed together with a small band in the fingerprint region and a major complicated absorption peak at 14 μm.

Polymerization of cyclooctadiene-1,5 gave in good yield a polymer (Table III) whose infrared spectrum showed a strong broad band centered at 3.4 μm with additional peaks at 3.5 and 3.3 μm. There was a broad unsaturation at 6.05 μm and a smaller broader absorption peak at 5.85 μm which might indicate some carbonyl absorption. A broad peak was centered at 6.9 μm with shoulders at 6.8 and 6.7 μm which were not well separated. Two additional broad peaks were found in the 9–10 μm region, a doublet at 14 μm and a singlet at 15 μm.

The polymer from *trans,trans,cis*-cyclododecatriene obtained in about 90% yield was a hard solid and shows a relatively simple and broad spectrum with a doublet at 3.35 to 3.5 μm; a small peak at 6.1 μm indicated unsaturation and broad peaks were also present at 6.9 and 7.4 μm. There was also an absorption at 10.2 μm which might indicate trans unsaturation and a broad absorption peak at 14 μm.

Norbornadiene [bicyclo[2.2.1]heptadiene] also gave a hard solid polymer of complicated structure whose main absorptions were at 3.4 μm with shoulders at 3.3 and 3.5 μm, a doublet at 6.1 μm, and also a doublet at 5.9 and 5.8 μm. Additional absorption peaks were a doublet at 6.8 and 6.9 μm, strong absorptions at 12.5 μm, and a doublet at 14.0 μm.

1-Methyl-1,4-cyclohexadiene was also polymerized in 93% yield by our high-pressure technique.

Polymerization of α-Olefins. Aliphatic α-olefins up to now have been polymerized to reasonably high mo-

Table IV
Polymerization of α-Olefins[a]

			anal.				
			calcd		found		
α-olefins	yield, %	remarks	C	H	C	H	
butene-1	80	colorless	85.63	14.37	85.89	14.21	$(C_4H_8)_n$
pentene-1	90, 45	colorless	85.63	14.37	85.64	14.14	$(C_5H_{10})_n$
isobutylene	90	colorless	85.63	14.37	85.98	14.49	$(C_4H_8)_n$
hexene-1	90	colorless	85.63	14.37	85.70	14.26	$(C_6H_{12})_n$
3-methylpentene-1	5	colorless					$(C_6H_{12})_n$
4-methylpentene-1	80	colorless					$(C_6H_{12})_n$
styrene	98	colorless	92.26	7.74	91.91	8.09	$(C_8H_8)_n$
α-methylstyrene	50	colorless	91.47	8.53	91.83	8.53	$(C_9H_{10})_n$
methyl methacrylate	80	insoluble	59.98	8.05	61.58	5.66	$(C_5H_8O_2)_n$

[a] Pressure 6 GPa, time 4 h, temperature 300 °C.

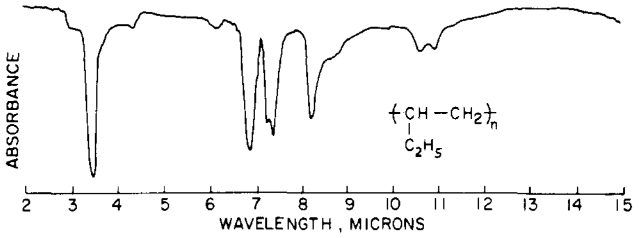


Figure 15. IR spectrum of poly(butene-1).

lecular weight only with coordination initiators or, in the case of isobutylene, with cationic initiators. We have succeeded in polymerizing these compounds in high yields to polymers of reasonable molecular weight with our high-pressure polymerization technique.

Butene-1 was polymerized in high yield (Table IV) to a soft solid poly(butene-1); this polymer was identical in its IR spectrum with an authentic sample prepared by coordination polymerization (Figure 15). **Pentene-1** gave a polymer in 90% yield whose infrared spectrum is also identical with a polymer obtained by coordination polymerization; the spectrum showed a triplet peak at 3.35, 3.45, and 3.55 μm with an additional small peak at 3.65 μm. A doublet was noticed at 6.85 and 6.90 μm with an additional sharp peak at 7.25 μm. The most characteristic peak of the spectrum is at 13.6 μm which is considered characteristic for paraffinic side chains.

Isobutylene gave also in good yield a polymer whose spectrum showed broad absorptions at 3.4–3.5 μm with a small peak at 3.75 μm, a big singlet at 6.8 μm, and a doublet at 7.2 and 7.35 μm (apparently caused by the gem-dimethyl group). Additional relatively strong peaks were found at 8.2 and 8.6 μm with a broad doublet at 10.5 and 10.8 μm. The IR spectrum of this polymer is identical with the IR spectrum of cationically prepared polyisobutylene. Polymers were also obtained from **3-methylpentene-1** (in relatively poor yield); a viscous grease was obtained from **2-methylbutene-1** by our high-pressure polymerization technique.

Excellent yields of good quality polymers **styrene** and **α-methylstyrene** were obtained at 6 GPa at temperatures of 300 °C and a reaction time of 4 h. Both polymers were completely soluble in benzene indicating that linear polymers were obtained under these reaction polymerization conditions and no cross-linking had occurred as was found for methyl methacrylate.

Polymerization of Internal Olefins. Homopolymerization of internal olefins without rearrangement has not yet been accomplished. Copolymerization, for example, of butene-2 with ethylene has however been known for a long time.[27] At least two accounts have been given on the homopolymerization of butene-2. The first report of a polymerization of butene-2 used acidic coordination initiators.[43] The polymer which was obtained by this method was later shown[44,45] to be poly(butene-1) as the butene-2 was isomerized to butene-1 which then underwent the normal coordination polymerization of α-olefins. In the second relevant report, the polymerization was described on clay which also is known to have acidic sites.[46] The polymer was obtained in trace amounts and was only characterized by an infrared spectrum. No further work was done with this polymer and no additional reports on this polymerization technique were recorded. The IR spectrum of this poly(butene-2) was reported but cannot be used as a conclusive assignment of a polymer structure.

A polymer which was considered the polymer of butene-2 and also may be called polyethylidene was prepared by polymerization of diazoethane.[47,48] The structure of this polymer contained substantial proportions of nitrogen and/or unsaturation.

Dimers and trimers of 2-methylbutene-2 and 2,3-dimethylbutene-2 have also been reported by high-pressure reactions of 2 GPa.[28,29]

Butene-2. *cis-* and *trans*-butene-2 were subjected to 6 GPa for 3 h at 350 °C. A viscous oil was obtained in good yield in each case. The infrared spectra of these polymers showed a strong band in the carbon–hydrogen frequency region at 3.4 and 3.5 μm with a small peak at 3.75 μm. Additional peaks were found at 6.9 and 7.25 μm. In addition, a broad peak was found at 10.0–10.5 μm and a broad but sharp peak centered at 12.5 μm. The spectrum of our poly(butene-2), especially in the fingerprint region, is completely different from the spectrum of the poly(butene-1) which is characterized by two strong peaks, one at 11.1 μm and a stronger one at 13.1 μm. The spectrum of our poly(butene-2) does not show any absorption peaks of this prominence and relative sharpness but a rather broad spectrum throughout the region of 8–15 μm, characterized by the peaks in the 10 and 12 μm region (Figure 16).

The ^1H NMR spectrum of poly(butene-2) showed a broad resonance at δ 0.9 with a smaller one at δ 1.2 assigned to the methyl methine protons, respectively (Figure 17).

It is remarkable that essentially identical infrared and ^1H NMR spectra were obtained from the polymers derived from either the *cis-* or *trans*-butene-2. Two explanations may be given for this phenomenon. It could be that either or both *cis-* and *trans*-butene-2 were isomerized to an equilibrium mixture of *cis-* and *trans*-butene-2 which then copolymerized giving the same general structure of the polymer. Another, and the more likely, possibility is that the growing polymer radical produced the same radical regardless of the stereochemistry of the monomer of the

Table V
Polymerization of Internal Olefins[b]

			anal. $(\text{-CH}_2\text{-})_n$			
			calcd		found	
olefins	yield, %	remarks	C	H	C	H
cis-butene-2	80	viscous oil	85.63	14.37	85.99	14.46
trans-butene-2	50	viscous oil	85.63	14.37	85.86	14.39
cis-pentene-2	73	viscous polymer	85.63	14.37	85.76	14.18
trans-pentene-2	60	viscous polymer	85.63	14.37	85.63	14.58
hexene-2	*a*	viscous oil				
2-methylbutene-2	*a*	viscous grease				
2,3-dimethylbutene-2	*a*	viscous oil				

[a] Yield was not determined. [b] Pressure 6 GPa, time 3 h, temperature 300 °C.

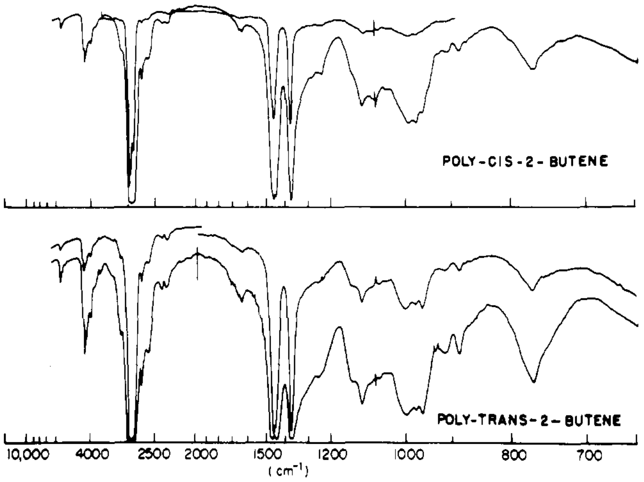


Figure 16. IR spectra of (a) poly(*cis*-butene-2) and (b) poly(*trans*-butene-2).

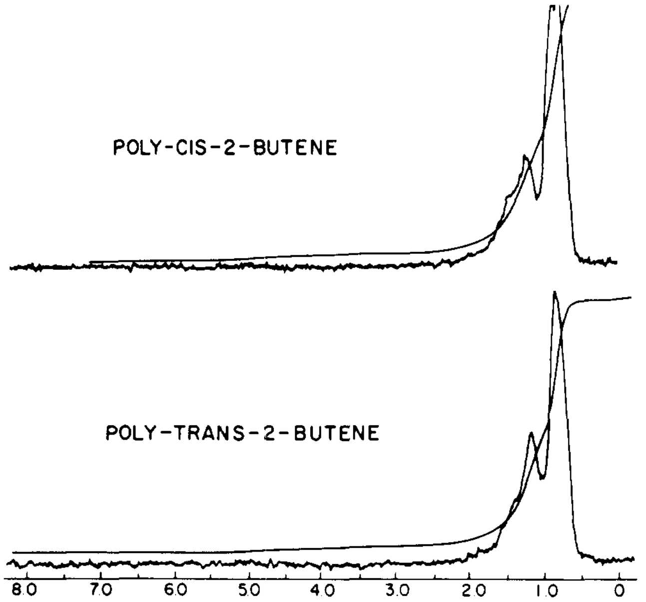


Figure 17. ^{1}H NMR spectra of (a) poly(*cis*-butene-2) and (b) poly(*trans*-butene-2).

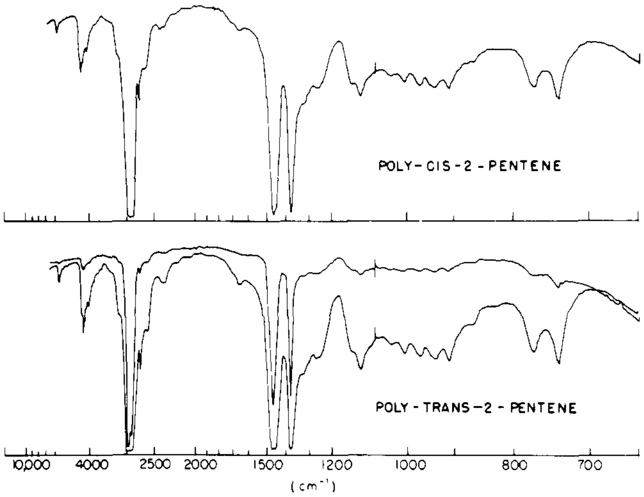


Figure 18. IR spectra of (a) poly(*cis*-pentene-2) and (b) poly(*trans*-pentene-2).

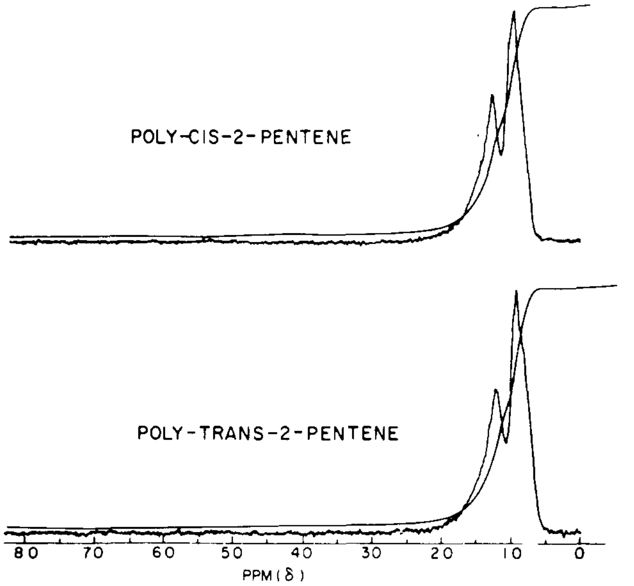


Figure 19. ^{1}H NMR spectra of (a) poly(*cis*-pentene-2) and (b) poly(*trans*-pentene-2).

stereochemistry of monomer addition.

Pentene-2. Both *cis*- and *trans*-pentene-2 were polymerized in 60–70% yield to spectrally indistinguishable, viscous polymers (Table V).

The infrared spectrum (Figure 18) indicated absorption peaks at 3.38, 3.42, and 3.48 μm with a small peak at 3.68 μm. Additional prominent absorption peaks were found at 6.8 and 7.25 μm and small and broad peaks at 8.9, 12.9, and 13.5 μm. A small but broad band at 11.2 μm could be caused by vinyl end groups. As in the case of butene-2 polymer, the IR spectra of the polymers from *cis*- and *trans*-pentene-2 are superimposable of each other indicating a great similarity in the structure of the two polymers. This is even more remarkable since in this case of the unsymmetric pentene-2 the possibility of H–H and H–T addition of the monomer units is also possible.

The ^{1}H NMR spectra (Figure 19) indicated that the main chemical resonance in poly(pentene-2) is at δ 0.9 with

Table VI
Polymerization of Dienes[b]

diene	temp, °C	yield, %	remarks	anal. calcd C	anal. calcd H	anal. found C	anal. found H
butadiene-1,3	25	15	white rubber	88.82	11.18	88.86	11.06
	150	50	black powder				
	300	60	black powder	$(-C_4H_6-)_n$			
2-methylbutadiene-1,3	25	22	white rubber (sol in benzene)	88.16	11.84	88.05	11.44
	150	30	black powder			93.69	6.31
	300	70	black powder	$(-C_5H_8-)_n$		87.90	5.92
2,3-dimethylbutadiene-1,3	300	90	white solid	87.73 $(-C_6H_{10}-)_n$	12.27	87.61	12.39
1-methylbutadiene-1,3	150	35	white solid	88.16	11.84	88.31	11.68
	300	*a*	black powder	$(-C_5H_8-)_n$			
2-chlorobutadiene-1,3	25	60	black powder				
	150	30	black powder				
	300	*a*	black powder				
2,3-dichlorobutadiene-1,3	25	50	black powder				
	150	20	black powder				
2-cyanobutadiene-1,3	300	30	black powder				

[a] Yield was not determined. [b] Pressure 6 GPa, time 4 h.

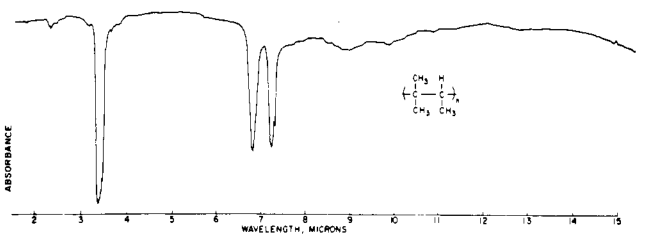


Figure 20. IR spectrum of poly(2-methylbutene-2).

a smaller peak at δ 1.2. As in the case of the infrared spectra of the polymer of *cis*- and *trans*-pentene-2, the ^1H NMR spectra of both polymers were superimposable.

Hexene-2 was also polymerized to a viscous oil. Its infrared spectrum is very similar to that of poly(pentene-2) and consists essentially of the three peaks at 3.4 μm to 3.5, 6.9, and 7.25 μm. The mass spectrum of this polymer shows it to be at least a hexamer. When hexene-2 was heated in the Monobloc to 300 °C for 4 h at 2.2 GPa, no polymer was obtained.

2-Methylbutene-2. This trisubstituted ethylene was polymerized to a viscous grease (Table V).

The infrared spectrum showed the major peak at 3.3 μm with a shoulder at 3.45 μm. In addition, peaks at 3.8 and 7.25 μm with a shoulder at 7.30 μm were observed. No additional peaks were observed in the infrared spectrum (Figure 20).

2,3-Dimethylbutene-2. Polymerization at 300 to 400 °C for 3 h at 6 GPa gave an oily viscous polymer which showed no unsaturation. In the IR spectrum of this polymer the main peak is at 3.4 μm with a shoulder at 3.45 μm. A small peak at 6.45 μm and the two major peaks at 6.8 and 7.25 μm with a shoulder at 7.30 μm were also observed. There are a few very small absorption peaks up to 11 μm when very thick sections of this polymer sample were studied but none were of structural significance (Figure 21).

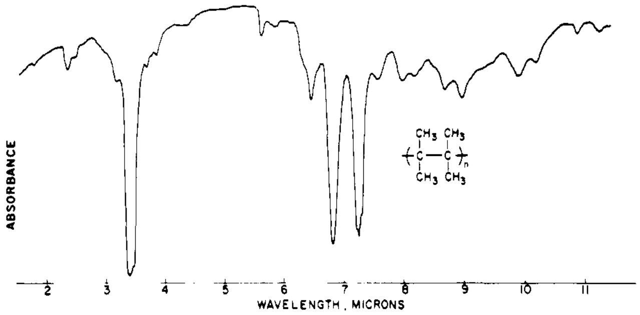


Figure 21. IR spectrum of poly(2,3-dimethylbutene-2).

Polymerization of Conjugated Linear Dienes. The polymerization of conjugated dienes has been carried out in the past by several methods. The study of the polymerization of dienes by the high-pressure technique is included in this study only to compare and describe the behavior of these compounds under these reaction conditions. It is not an attractive way to prepare polydienes. Most dienes (Table VI) exposed to 6 GPa at elevated temperatures flashed and gave black insoluble powders which are apparently highly carbonized residues. An elemental analysis for the polymer of isoprene was calculated as $(C_5H_4)_n$ instead of $(C_5H_8)_n$. No characteristic infrared spectrum could be obtained from such a polymer. A 15% yield of polybutadiene which was a white elastomer and completely soluble in benzene was obtained at room temperature and 6 GPa. A white elastomer, soluble in benzene, was also obtained in 22% yield from isoprene when the reaction was carried out at room temperature. Only 2,3-dimethylbutadiene-1,3 could be polymerized in high yield to a white solid at 300 °C and 6 GPa. A 35% yield of a white solid was also obtained from 1-methylbutadiene-1,3.

Miscellaneous Reactions. A few monomers of varied structure including cyclic monomers capable of ring-opening polymerization were subjected to 6 GPa. Of the cyclic ethers, only trioxane gave in quantitative yield at 300 °C reaction temperature the well-known polyoxymethylene. Epichlorohydrin and propylene oxide decomposed in an exothermic reaction as high pressure was applied.

1-Cyanobicyclo[3.1.0]hexane, when subjected to 300 °C and 6 GPa, gave in apparently quantitative yield a brownish polymer which seems to be based on ring-opening polymerization of the three-membered ring. The polymer had the following analysis. Calcd: C, 78.46, H, 8.47, N, 12.07. Found: C, 78.72, H, 8.90, N, 12.36. 1-Cyanobicyclobutane derivatives [1.1.0] have been known to polymerize primarily by the radical mechanism.[49]

A brownish solid was obtained which apparently was not carbon when cyclooctatetraene was subjected to 6 GPa for

3 h at 100 °C. This polymer was not further characterized.

Two carbonyl compounds, chloral and hexafluoroisobutyraldehyde, when subjected at 100 °C for 3 h and 6 GPa did not polymerize and the individual products were entirely recovered as the monomers. These results seem to confirm that our polymerizations at 6 GPa and 300 °C are radical reactions because it is known that these aldehydes polymerize easily but only by ionic mechanisms.[50,51]

Conclusions

Pressures of 6 GPa produced in a tetrahedral anvil apparatus polymerized for the first time a number of monomers. New 1,2 polymers were obtained from cyclopentene, cyclohexene, cycloheptene, cyclooctene and cyclodocene, 1-methylcyclopentene, 1-methylhexene, 3-methylcyclohexene, 4-methylcyclohexene, 1-phenylcyclohexene, 1-methylcycloheptene, 3-methylcyclooctene, *cis*- and *trans*-butene-2, and hexene-2. Attempted polymerization of 2-methylbutene-2 and 2,3-dimethylbutene-2 had previously given only dimers and trimers. All polyolefins gave solid polymers by the high-pressure method which seems to proceed by a radical mechanism. Some of these polymers can only be made by coordination initiators or gave oligomers by radical polymerization.

1-Cyanobicyclo[3.1.0]hexane polymerized apparently by opening of the cyclopropane ring. Cyclic dienes, such as cyclohexadiene-1,3, cyclohexadiene-1,4, 1-methylcyclohexadiene-1,4, cyclooctadiene-1,5, and norbornadiene polymerized to cyclic polymers. Polymerization of these monomers had been accomplished in the past.

Soluble apparently noncross-linked polymers were obtained under low-temperature conditions from butadiene, 2-methylbutadiene, and 4-methylbutadiene. Under normal high-pressure reaction conditions at 6 GPa and 300 °C a flash reaction occurred which gave black powder of high carbon content. 2,3-Dimethylbutadiene polymerized under the normal polymerization conditions.

Carbonyl compounds, such as chloral and hexafluoroisobutyraldehyde, did not polymerize, but trioxane gave in quantitative yield polyoxymethylene.

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