

Radiation-Induced Polymerization at High Pressures*

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INTRODUCTION

Radiation from cobalt-60 is capable of initiating the polymerization of many substances. For the study of polymerization at high pressures and various temperatures it has many practical and theoretical advantages. Relatively simple apparatus may be used since no special windows for the radiation are needed, as would be necessary if one were to carry out high pressure polymerization using ultraviolet light. *A priori* one anticipates that the rate of initiation will be essentially independent of pressure as well as temperature.

For most elementary reactions of the bimolecular type there is a net decrease in volume upon the formation of the transition complex. On this basis reaction rates increase with the application of pressure. In polymerization systems there are usually competing reactions, propagation, transfer, and often other side reactions. The first favors high polymer production, while the latter two favor low molecular weight products. High pressure investigation of polymerization is a feasible method for determining which of the competing reactions are most influenced by pressure and hence which have the greater volume decreases in the transition complex.

In this work several monomers that are normally not polymerized by free radicals were studied. The most intensively investigated monomers were propylene, perfluoroheptene-1, and carbon disulfide. Other monomers studied were trifluorovinyl phenyl ether, trifluorovinyl pentafluorophenyl ether, and 4-chloroperfluoroheptadiene-1,6. Some preliminary results indicate that carbon monoxide and carbon dioxide can be copolymerized with tetrafluoroethylene.

EXPERIMENTAL

The polymerization procedure consisted of filling an appropriate pressure vessel with monomer, usually degassed, and exposing the vessel to radiation from a Co⁶⁰ source. Two Co⁶⁰ sources were used, one of 1200 curies which can be used to give the sample in the pressure vessel a maximum average

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dose rate of 0.13 Mrad/hr., and one of 50,000 curies capable of giving the sample a dose rate of 3 Mrad/hr.

The pressure vessels are simple cylinders, made of hardened steel or beryllium copper, in which pressure is applied to about 17 cc. of sample by means of a piston pushed by a hydraulic ram. A threaded cap follows the piston and holds it in the vessel so that the vessel can be removed from the press and irradiated without losing pressure. While in the press, the vessel is brought to the desired temperature, which is maintained constant within 1°C. by a proportionating controller. The pressure is then adjusted before removal of the vessel from the press. The pressure in the vessel is calculated from the oil pressure in the hydraulic system of the press. Approximate corrections are applied for piston friction and cap distortion. The vessels can be used continuously for experiments at pressures of 10,000–15,000 atm. At higher pressures their useful life is shortened.

The most critical part of the pressure system is the seal which prevents the contents of the vessel from leaking past the piston. A Bridgman-type seal¹ was used. The materials and design of the seal were modified in order to minimize the friction between the cylinder wall and the piston.

RESULTS

The rates of polymerization were determined by dividing the conversion by time. The conversions were relatively low in the range 0–20%. Low molecular weights were determined with a vapor pressure osmometer or by means of viscosity measurements. Intrinsic viscosities of the high molecular weight polymers were usually obtained if the polymers were soluble.

The polymers produced had maximum degrees of polymerization around 75. At low radiation intensities rates of polymerization at constant pressure for both monomers varied linearly with the square root of the intensity. However, at intensities above 0.01 Mrad/hr. the rates of polymerization dropped off. This effect appears to be explainable by the premise² that the rate of initiation is large enough to result in termination of many of the growing radicals by primary radicals.

The degree of polymerization of polypropylene from experiments at 14,600 atm. and 21°C. was essentially independent of the rate of polymerization. The inherent viscosities of many of the polypropylene samples were measured in decalin at 135°C. The viscosity-average degree of polymerization, \overline{DP}_v , was calculated by using the relation of Chiang.³ The maximum inherent viscosity of our samples was 0.11, whereas the minimum value in his calibration is 1.5. Qualitatively the changes in \overline{DP}_v with reaction conditions parallel those in \overline{DP}_n , but the calculated \overline{DP}_v is as much as four times \overline{DP}_n . This ratio is not firmly fixed owing to the uncertainty of the extrapolation.

Infrared spectra of the polypropylenes are more like those of molten Ziegler-Natta polymers than the products of the low-temperature acid-

catalyzed polymerization.⁴ There is evidence that propyl and vinyl groups are present in small amounts. This presumably reflects the relatively low molecular weight of our polymers. Terminal ethyl groups do not seem to be present.

The polypropylenes range from faintly colored materials similar to the low molecular weight polyisobutylene oils to opalescent gums so viscous that they retain impressions for several days. The latter gums have the higher molecular weights. All the polypropylenes are soluble in benzene at room temperature. Sometimes the solutions are opalescent, but they pass through coarse frits without loss of polymer or opalescence.

At a constant pressure of 17,100 atm. and 139°C. the reciprocal degree of polymerization versus rate of polymerization behavior of the polyperfluoroheptene allowed one to estimate a transfer constant of 0.023 to 0.032 and a $G(i)$, radicals per 100 e.v. of absorbed energy, of 16 to 7 assuming disproportionation. Assuming the G value for initiation to be independent of pressure, one can estimate the other transfer constants from one or two experiments at different pressures. Experimental results are shown in Table I.

Trifluorovinyl pentafluorophenyl ether and 1,1,2-trifluorovinyl phenyl ether have been prepared in our laboratories and have not been polymerized by the normal free-radical methods. At 12,000 atm., 100°C., and 0.0032

TABLE I
n-Tetradecafluoroheptene-1 Rates and Polymer Characterization^a

Pressure, atm. \times 10^{-3}	Temp., °C.	$10^6 R_p$, hr. ⁻¹	DP_n	(k_3/k_2)
8.1	97	23.5		
8.1	125	54.5		
8.1	146	73.9		
8.1	168	40.9		
11.9	93	88		
11.9	140	378	42 ± 2	negative to 0.005 ^b
11.9	166	521		
11.9	183	486		
11.9	237	2.5		
17.1	94	109	19 ± 1	
17.1	139	1047	26 ± 1	0.023-0.032
17.1	189	3760	76 ± 8^c	
17.1	211	6113	52 ± 2	0.016-0.018 ^b
17.1	267	7240	17 ± 1	
17.1 ^d	140	2.9		
17.1 ^d	214	241	30 ± 1	

^a Dose rate = 0.0027 Mrad/hr. unless specified.

^b Low value assumes $G(i) = 16$ with disproportionation; high value assumes $G(i) = 7$ with disproportionation.

^c Polymer subjected to prolonged evacuation before measuring DP_n .

^d Thermal polymerization.

Mrad/hr. the trifluorovinyl pentafluorophenyl ether gave 2.7% conversion to polymer. The $G(M)$, G value for monomer consumption, was 283. Similar experiments on 1,1,2-trifluorovinyl phenyl ether are summarized in Table II. Large $G(M)$ values were attained; however, the intrinsic viscosities indicate relatively low molecular weights.

TABLE II
Polymerization of 1,1,2-Trifluorovinyl Phenyl Ether

Pressure, atm. $\times 10^{-3}$	Temp., °C.	Dose rate, Mrad/hr.	$10^4 R_p$, hr. ⁻¹	$G(M)$, molecules/ 100 e.v.	$[\eta]$, dl./g.
6.4	102	1.06	2810	14	0.03
10.0	191	0.0027	— ^b	0	—
14.0	145	0.0027	236	455	0.026
$\sim 14.0^a$	103	0.0027	687	1190	0.03

^a Monomer freezes at 6,400 atm. at this temperature. Pressure may not have been uniform.

^b Very high yield of material tentatively identified as dimer.

TABLE III
Polymerization of 4-Chloroperfluoroheptadiene-1,6

Pressure, atm.	Temp., °C.	Time, hr.	Dose rate, Mrad/hr.	Conver- sion, %	$[\eta]$, dl./g.
~ 1	150	71	0.2	100	0.09
~ 1	100	71	0.2	60	0.05
< 1	30	504	0.2	45	0.04
~ 1	160	336	U.V.	50	0.04
1.36×10^4	147	113	0.003	100	0.60

Another fluorocarbon monomer studied was 4-chloroperfluoroheptadiene-1,6. Results of the study are shown in Table III. Polymerization of the degassed monomer in sealed evacuated tubes gave a product of low molecular weight, as indicated by the low intrinsic viscosity. These materials are clear brittle solids of poor physical properties. The material produced under high pressure with $[\eta] = 0.60$ dl./g. is, on the other hand, a tough flexible material.

Carbon disulfide has been polymerized previously^{1,5} by heating the liquid to temperatures of 185°C. or greater at pressures of the order of 55,000 atm. to give a black solid; its infrared spectrum⁵ suggests that a good portion of material has the structure

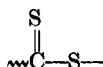


Table IV summarizes our results. It is believed that gamma radiation facilitates this polymerization. The material formed at 1 atm. is a tan

TABLE IV
Polymerization of Carbon Disulfide

Pressure, atm. $\times 10^{-3}$	Dose, Mr ^a	Temp., °C.	Yield, %	$G(M)$
0.001	211	62	0.95	0.65
4	221	66	0.86	0.60
10	400	98	4.1	1.5
10	153	100	1.46	1.4
14	149	66	1.3	1.3
15	18	20	0.15	1.0 ^a

^a Dose rate 0.13 Mrad/hr.; all other 3.2 Mrad/hr.

color and is believed to be mainly decomposed carbon disulfide. The material produced at high pressure is definitely a deep black. The $G(M)$ values are low, but show a definite increase with temperature and pressure. The polymer is not soluble in monomer though it appears to be highly swollen with its monomer. Upon thermal decomposition in a vacuum system, about 30% of the polymer is converted back to liquid carbon disulfide. The rest of the polymer is converted to complex sulfur-carbon compounds and an apparently carbon residue.

DISCUSSION

Polypropylene

The results on the polymerization of propylene are readily interpreted within the framework of accepted free-radical polymerization mechanisms. Since the DP is independent of the rate of polymerization at a given pressure and temperature, we assume that $DP_n = k_2/k_3$, the ratio of the propagation constant to the monomer transfer constant. The variation of DP_n and rate of polymerization with pressure is given in Figure 1. Since the DP increases with pressure rather less than the rate, it is evident that both the propagation and the monomer transfer constant are increasing with pressure. Plotting the log of the rates and DP versus reciprocal temperature at a given pressure, on the basis of transition state theory for absolute rates, allows one to estimate the enthalpy differences for the reactants going to the activated states. Taking our gamma-ray initiated rates of polymerization to be given by:

$$-dM/Mdt = (k_i/2k_4V)^{1/2}k_2$$

where k_i , the fractional rate of initiation, equals $G(i)Im/N100$, N being Avogadro's number, m the molecular weight of the monomer, I the radiation intensity in electron volts of absorbed energy per gram per second, $G(i)$ the yield of initiating radicals per 100 e.v. of absorbed energy, and V the molar volume of monomer. If $G(i)$ is taken to be independent of temperature, the rate constants for propagation, k_2 , and termination, k_4 , are the only quantities dependent on temperature. From the temperature dependence

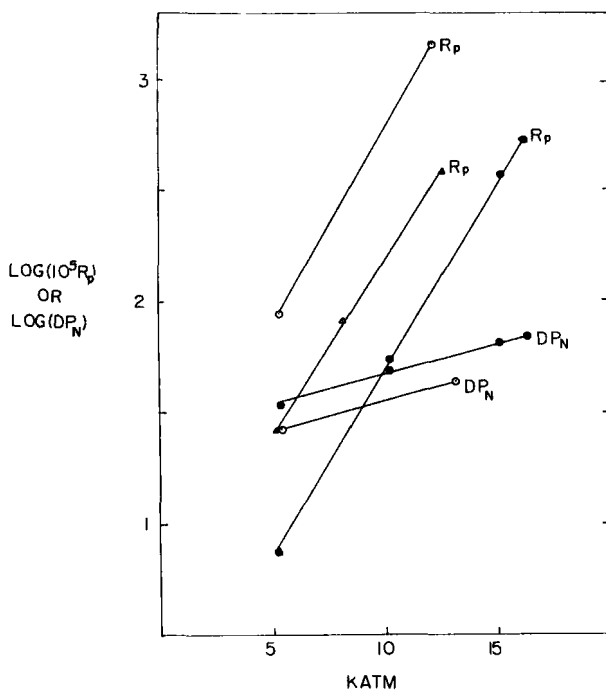


Fig. 1. Polymerization of propylene. Variation of rate of polymerization R_p and number-average degree of polymerization with pressure at a radiation dose rate of 0.0031 Mrad/hr.: (O) 83°C.; (Δ) 48°C.; (\bullet) 21°C.

of the rate, we can then estimate $\Delta H_2^* - (\Delta H_4^*/2)$. Knowing the dose rate I and assuming $G(i)$ to be 1, $\Delta S_2^* - (\Delta S_4^*/2)$ can be estimated. $G(i)$ is also assumed to be independent of pressure. Taking $G(i)$ as 10 would not change the estimates greatly; measured $G(i)$'s for unsaturated hydro-

TABLE V
Thermodynamic Quantities in Rate of Polymerization
Expressions for Propylene

Pressure, K atm.	Form of sum ^a	ΔF^* , cal./mole	ΔH^* , cal./mole	ΔS^* , cal./mole-°C.
5.0	$\Delta_2^* - (\Delta_4^*/2)$	15,860	7,800	-27.3 ^b
12.0	$\Delta_2^* - (\Delta_4^*/2)$	14,450	8,160	-21.4 ^b
16.4	$\Delta_2^* - (\Delta_4^*/2)$	13,270	8,400 ^c	-16.6 ^b
5.0	$\Delta_2^* - \Delta_3^*$	-2,070	-855	4.13
12.0	$\Delta_2^* - \Delta_3^*$	-2,330	-760	5.34
16.4	$\Delta_2^* - \Delta_3^*$	-2,500	-700 ^c	6.12

^a Each thermodynamic function to the right is made up of elements having the form defined in this column.

^b Assumed that $G(R) = 1$.

^c By extrapolation of values at 5 and 12 K atm.

carbons are normally in this range of values. Table V contains the estimated values of the thermodynamic quantities. From the DP data, estimates of $\Delta H_2^* - \Delta H_3^*$ and $\Delta S_2^* - \Delta S_3^*$ were also made and are presented in Table V.

The variation of $\log DP_n$ with pressure P at constant temperature for our system is:

$$\log DP_n = \frac{(-\Delta V_2^* + \Delta V_3^*)P}{2.3RT} + C_1$$

Also

$$\log R_p = \left[\frac{-\Delta V_2^* + (\Delta V_4^*/2)}{2.3RT} \right] P + C_2$$

Here C_1 and C_2 are integration constants. The slopes in Figure 1, therefore, may be used to calculate the sums of the ΔV^* 's. The sum $(\Delta V_2^* - \Delta V_3^*)$ is -1.57 cc./mole at 21°C . and -1.67 cc./mole at 83°C . The sum $(\Delta V_2^* - \Delta V_4^*/2)$ in cc./mole is: -9.62 at 21°C ., -9.64 at 48°C ., and -12.12 at 83°C .

Perfluoroheptene-1

The radiation-induced polymerization of perfluoroheptene at various pressures between 8,000 and 17,000 atm. is also best treated within the framework of a free-radical mechanism. However, it seems that at the highest temperatures studied a back reaction occurs, as can be seen by the three upper full-line curves in Figure 2, which is a plot of $\log R_p - 0.5 \log T$ versus the reciprocal of the absolute temperature. The $0.5 \log T$ results from the temperature dependence of the preexponential terms in the absolute rate as applied in this case using the usual free-radical mechanism for polymerization. By introducing a depropagation step in the free-radical polymerization mechanism, the rate expression becomes

$$-dM/Mdt = (k_i/2k_4V)^{1/2} (k_2 - k_{-2}M^{-1})$$

If no back reaction occurs, the log plots in Figure 2 should follow the dotted extension of the straight portions of the full lines. The difference in rate between the dotted lines and the full lines is assumed to be the rate of back reaction or depolymerization. At the intersection of the dotted and dashed lines the rate of polymerization equals the rate of depolymerization. The temperature at these intersections is then by definition the ceiling temperature. From the data in Figure 2 one estimates the thermodynamic quantities in the absolute rate expressions. These are given in Table VI. They do not depend strongly on the value assumed for $G(i)$. From the DP_n measurements at 17,100 atm. and 139°C ., $G(i)$ was estimated to be in the range 7–16 if termination was by disproportionation of radicals, or 14–32 if termination was by combination of radicals. For the purpose of calculating the values presented in Table VI, $G(i)$ was taken to be 25.

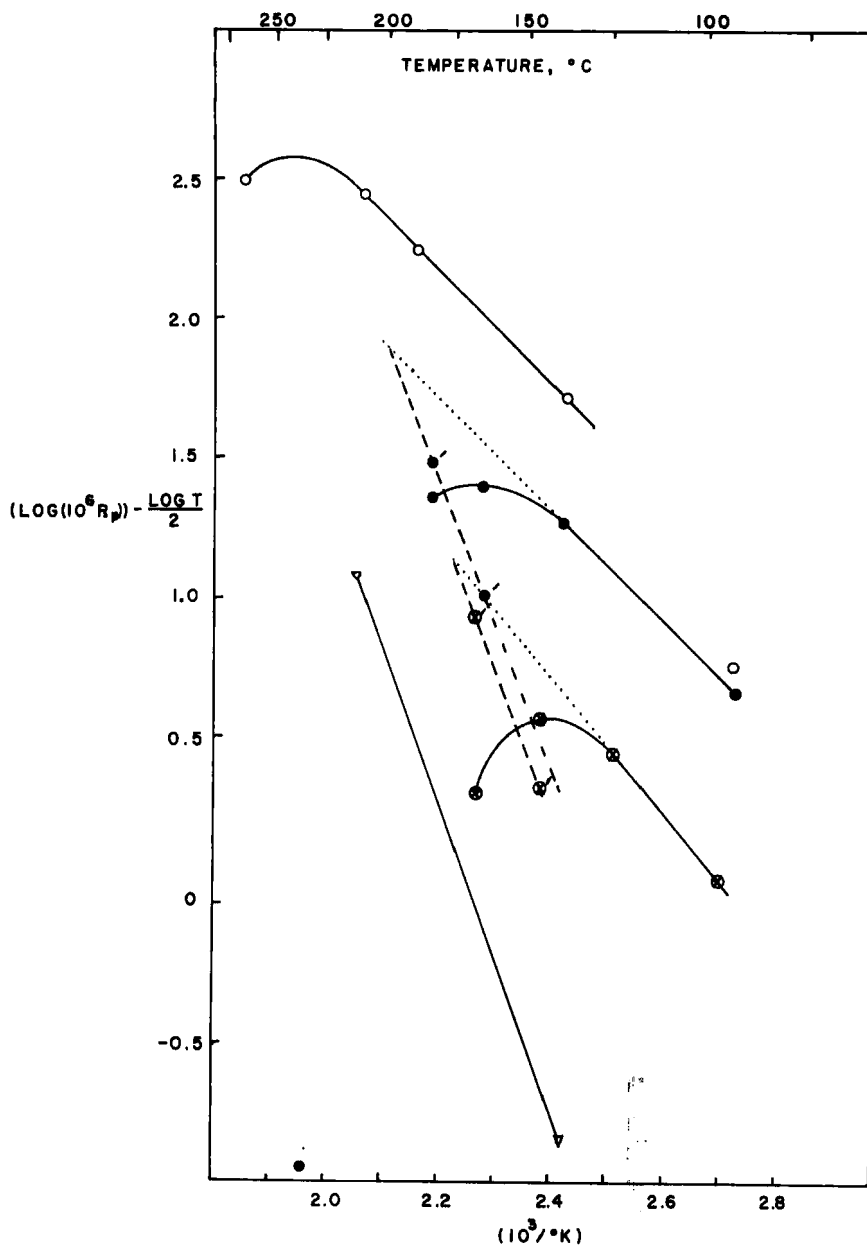


Fig. 2. Polymerization of *n*-Perfluoroheptene-1. Variation of rate of polymerization with temperature: (O) 17,100 atm., dose rate 0.0027 Mrad/hr.; (●) 11,900 atm., dose rate 0.0027 Mrad/hr.; (⊗) 8,100 atm., dose rate 0.0027 Mrad/hr.; (∇) 17,100 atm., thermal polymerization. Full lines (—) indicate polymerization; dashed lines (--) indicate depolymerization; points with primes are for the depolymerization reaction; intersection of dotted and dashed lines gives the ceiling temperature.

The plot of $\log R_p$ versus pressure was curved. This indicates a changing value of $\Delta V_2^* - 0.5\Delta V_4^*$ with pressure. This volume term for polymerization at 139°C. was estimated to be < -13.6 cc./mole at 8,100 atm., -9.4 cc./mole at 11,900 atm., and > -6.8 cc./mole at 17,100 atm.

TABLE VI
Thermodynamic Quantities in Rate of Polymerization
Expressions for Perfluoroheptene-1^a

Pressure, Reaction atm. $\times 10^{-3}$	Temp., °C.	ΔF^* cal./mole	ΔH^* , cal./mole	ΔS^* , cal./mole-°C.
Polymerization				
8.1	139	18640	10500	-19.8
11.9	139	17500	9070	-20.5
17.1	139	16630	9560	-17.1
17.1	189	17500	9560	-17.2
Depolymerization				
8.1	139	19500	21900	5.8
11.9	139	19230	21500	5.5

^a Each thermodynamic quantity is made up of elements having the form $\Delta_2^* - 0.5\Delta_4^*$.

Since we have in Table VI the differences of the thermodynamic quantities between the reactants and the transition complex for both polymerization and depolymerization of perfluoroheptene-1 at two pressures, we can,

TABLE VII
Thermodynamics of Polymerization at 139°C.
for Perfluoroheptene-1

Pressure, atm. $\times 10^{-3}$	ΔF , cal./mole	ΔH , cal./mole	ΔS , cal./mole-°C.	T_c , °C. ^a
8.1	-760	-11400	-25.6	172
11.9	-1730	-12430	-26.0	205

^a T_c in °K. = $(\Delta H/\Delta S)$.

by taking the differences of these quantities, obtain the free energy, entropy, and enthalpy for the overall polymerization process at each of the two pressures. These data and the ceiling temperatures at the two pressures are given in Table VII.

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Synopsis

Several radiation-induced polymerizations reactions were investigated at pressures between 5,000 and 17,000 atmospheres and temperatures between 20 and 275°C. The most detailed studies have been with propylene and *n*-tetradecafluoroheptene-1. With both monomers the variation of rate of polymerization, R_p , with temperature and radiation intensity is consistent with a free radical mechanism. The maximum number of monomer units converted to polymer per 100 e. v. absorbed, $G(M)$, is 108,000 and 7,600 in the polymerization of propylene and the heptene, respectively; thus, the kinetic chains are long. However, the number-average degree of polymerization, DP_n , is low, the maximum values being about 75 in both polymerizations. In the polymerization of propylene, transfer to monomer limits DP_n ; the transfer constant becomes greater as temperature increases or pressure decreases. In the polymerization of the heptene, DP_n is determined by both transfer and termination. In the latter polymerization both R_p and DP_n first increase and then decrease as the temperature is raised at constant pressure because the depolymerization rate becomes appreciable at high temperature and reduces the observed R_p .

Résumé

De nombreuses réactions de polymérisation induites par les radiations ont été étudiées à des pressions comprises entre 5.000 et 17.000 atmosphères et à des températures comprises entre 20°C et 275°C. Les études les plus détaillées ont été effectuées sur le propylène et le *n*-tétradécafluoroheptène-1. Pour ces deux monomères, la variation de la vitesse de polymérisation R_p en fonction de la température et de l'intensité des radiations implique un mécanisme radicalaire. Le nombre maximum d'unités monomériques converties en polymère pour une absorption d'énergie de 100 électron-volts, $G(M)$ est de 108.000 et de 7.600 respectivement dans la polymérisation du propylène et de l'heptène; donc les chaînes cinétiques sont longues. Cependant le degré de polymérisation moyen en nombre DP_n est bas, la valeur maximum étant de 75 dans les deux polymérisations. Dans la polymérisation du propylène, le transfert sur monomère limite DP_n ; la constante de transfert devient plus importante quand la température augmente ou quand la pression diminue. Dans la polymérisation de l'heptène DP_n est déterminé à la fois par les réactions du transfert et de terminaison. Dans cette dernière polymérisation, R_p et DP_n commencent tous deux par augmenter et puis diminuent ensuite lorsqu'on augmente la température à pression constante parce que la vitesse de dépolymérisation devient appréciable à température élevée et abaisse la valeur observée de R_p .

Zusammenfassung

Es wurden mehrere Strahlungspolymerisationsreaktionen bei Drucken zwischen 5000 und 17000 Atmosphären und Temperaturen zwischen 20°C und 275°C untersucht. Die eingehendsten Untersuchungen wurden an Propylen und *n*-Tetradekafluorhepten-1 durchgeführt. Bei beiden Monomeren steht die Änderung der Polymerisationsgeschwindigkeit R_p mit Temperatur und Strahlungsintensität mit einem radikalischen Mechanismus in Einklang. Die maximale Zahl der pro 100 eV absorbiertener Energie umgesetzten Monomermoleküle, $G(M)$, ist bei der Polymerisation von Propylen bzw. des Heptens 108000 bzw. 7600, d.h. die kinetischen Ketten sind lang. Das Zahlenmittel des Polymerisationsgrades, DP_n , ist jedoch niedrig, u.zw. in beiden Fällen maximal etwa 75. Bei der Polymerisation von Propylen wird DP_n durch Übertragung mit dem Monomeren begrenzt. Die Übertragungskonstante nimmt mit steigender Temperatur und abnehmendem Druck ab. Bei der Polymerisation des Heptens wird DP_n sowohl durch Übertragung als auch durch den Abbruch bestimmt. Bei der letzteren Polymerisation nehmen sowohl R_p als auch DP_n zuerst zu und sinken dann beim Ansteigen der Temperatur bei konstantem Druck, da bei hoher Temperatur die Depolymerisationsgeschwindigkeit von merklicher Grösse wird und das beobachtete R_p erniedrigt.