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Radiation Polymerization of Hexachlorocyclotriphosphazene

H. Q. Liu and V. T. Stannett*

Department of Chemical Engineering, North Carolina State University, Raleigh, North Carolina 27695-7905. *Received February 13, 1989; Revised Manuscript Received May 31, 1989*

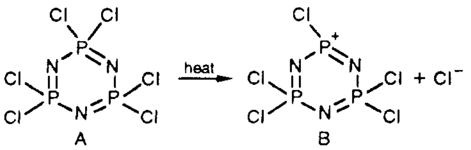
ABSTRACT: The effect of extensive purification and extremely rigorous drying on the radiation-induced polymerization of hexachlorocyclotriphosphazene in bulk has been investigated. In the solid state only slightly higher yields of polymer were found compared with those previously reported. In the melt, however, polymerization took place when extremely dry and pure monomer was irradiated. The corresponding thermal experiments resulted in essentially zero polymerization. This is the first time radiation polymerization of the trimer in the liquid state has been observed. The irreproducibility of the conversions coupled with the low molecular weights of the polymers led to a more detailed study in decalin solution. Good yields of polymer with satisfactory reproducibility were obtained. The conditions of purification and drying were found to have a profound effect on the rates. The order of the rates on the trimer concentration was about 3/2, consistent with the proposed mechanism. The molecular weights were, however, low—similar to those found in the bulk melt. This was ascribed to chain transfer by the proposed unpaired cationic propagating chains. The effect of adding a bulky, electron acceptor, pyromellitic dianhydride, was investigated. Much higher rates and higher molecular weights were obtained. This is believed to be due to the role of ion pairs as originally reported and discussed by Hayashi with the radiation polymerization of α-methylstyrene in solution. The corresponding trifluoroethoxy polymers were all soluble, substantially free from higher rings and about 450 000 at the GPC peak. The glass temperature of the trifluoroethoxy polymer was −66 °C in agreement with the literature values. The activation energy for the polymerization was about 43 kcal/mol, similar to those reported for the BCl_3 polymerizations.

Introduction

The polyphosphazenes represent a unique class of polymers with a completely inorganic backbone. They can be highly flame retardent, biocompatible, and chemically resistant and have good high-temperature resistance. Excellent reviews have been published regarding these polymers.[1-5] Although alternative routes for their synthesis have been presented,[5,6] the most attractive still is the polymerization of hexachlorocyclotriphosphazene. High molecular weight products can be obtained, and the chlorines can readily be substituted to give a wide variety of structures. Early work tended to give cross-linked polymers, but a real breakthrough occurred when Allcock et al. demonstrated that at lower conversions high molecular weight soluble poly(dichlorophosphazene) could be obtained from which stable poly(organophosphazenes) could be prepared.[7-9]

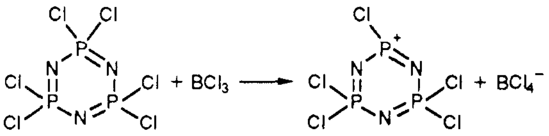
The polymerization of the trimer has been extensively studied over many years. The earlier work has been summarized by Allcock,[10] Hagnauer,[11] and Singler et al.[12] Thermal polymerization at above 220 °C has been the main process studied, but more recently the use of Lewis acids and other catalysts has been emphasized.[13-15] In all of these studies the strong dependence on temperature and the pernicious influence of even trace amounts of impurities has often led to a disconcerting lack of reproducibility. Nevertheless important advances in our understanding of the polymerization mechanism have been made.

It now seems clear that the thermal process is cationic in nature and the initiation step is



(1)

With Lewis acid initiation such as with boron trichloride, much studied by Sennett et al.,[13] it is simplest to assume the initiation to be



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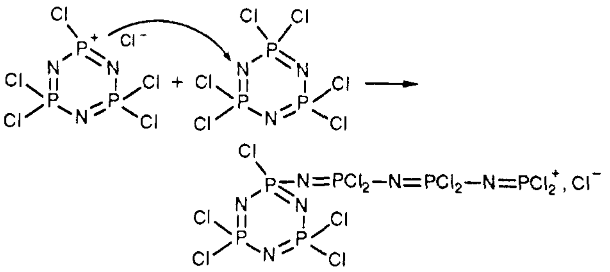
However, a ring opening mechanism has also been proposed by Sennett et al.[13] together with some supporting evidence. The nature of the end groups in both thermal and catalyzed initiation still appears to be uncertain. The polymerization reaction is, most simply



(3)

High-energy radiation is known to initiate cationic polymerization in the solid state and, under extremely pure and dry conditions, in the liquid state. Early work by Caglioti et al.[16] and Cordischi et al.[17] showed that polymerization of the trimer to cross-linked materials took place in the solid state with the rate increasing up to the melting point and then dropping to zero. A rather analogous situation was found with hexamethylcyclotrisiloxane. This monomer was also found to polymerize in the solid but not in the liquid state.[18] More recently, however, bulk liquid polymerizations were achieved when the monomers were rigorously dried.[19-21]

This paper is concerned with the application of this approach to the radiation polymerization of hexachloro-

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* To whom correspondence should be addressed.

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cyclotriphosphazene (HCP) in the liquid melt state and in solution. In principle the initiation step could be similar to eq 1 but with radiation rather than heat. Some interesting related results have recently been reported with mass spectra and plasma polymerization.[22,23]

Experimental Section

The hexachlorocyclotriphosphazene used was Phosnic 390 from the Nippon Fine Chemical Co., Ltd. The trimer was first of all recrystallized for various times from heptane that had been dried over CaH_2. The traces of solvent remaining in the monomer, after recrystallization, were removed by repeated sublimation under high vacuum ($<10^{-5}$ Torr). The superdried monomer was then prepared by drying it over BaO which has been baked under high vacuum (10^{-6} Torr) at 400 °C for 1 day. For having a good contact between the monomer and the drying agent, the monomer was kept in the liquid state during this procedure. The transfer of samples into ampules or NMR tubes was all carried out under high vacuum by sublimation. Rather elaborate systems with break seals and grease-free stopcocks were used throughout. A number of our experiments were carried out in NMR tubes.

Tetrahydrofuran (THF) (Fisher) was distilled from sodium under N_2. The trifluorethanol (Aldrich) was used as received.

Decalin (Aldrich) was dried over CaH_2 under vacuum and then over four sodium mirrors. It was dried over one more sodium mirror again just before being introduced into the polymerization tubes.

Pyromellitic dianhydride (Aldrich 99%) was transferred into a glass tube equipped with a Teflon stopcock and a break-seal in a drybox under N_2 and then sealed off under vacuum. It was sublimed once under dynamic vacuum before being transferred into the polymerization tubes by sublimation.

The glass vessels used in the experiments had been baked at 400 °C under high vacuum (10^{-6} Torr). The high polymerization temperature was obtained by using a special oil bath in the chamber of the cobalt-60 γ-ray source. The radiation source used was a Gammacell 220, Atomic Energy of Canada Ltd. The dose rate of the γ-ray source was about 0.1 Mrad/h.

The conversions was determined in two ways, by subliming out the residual monomer after polymerization or by ^{31}P NMR in which case the polymerization was carried out in sealed NMR tubes. Phosphorus ^{31}P NMR spectra were obtained on an IBM AC-100 MHz NMR spectrometer at 90 °C within sealed 5-mm NMR tubes in decalin. Aqueous H_3PO_4 was used as an external standard. The intrinsic viscosities of the (fluoroethoxy)polyphosphazenes were measured with a Ubbelohde type viscometer at 30 °C in THF. Gel permeation chromatograms were obtained by using a Waters 150C GPC machine at 40 °C. The column was a PLGel 10μ mixed 30-cm column from Polymer Laboratories Inc. THF was used as the elution solvent. The polymer obtained was converted to the fluoroethoxy polymer using the methods described by Allcock.[24]

Results and Discussion

Initially the early (1962) results obtained by Caglioti et al.[16] in the solid state were repeated with the superdried trimer. The results are shown in Figure 1 together with the best results obtained in the melt and in decalin solution. The early solid-state results were only slightly improved by superdrying; however, polymerization was clearly achieved in the melt and in concentrated solution in dry decalin. Interestingly the effect of superdrying became clear closer to the melting point where some molecular mobility was presumably present. It is believed that, as in the case of the cyclic hexamethylsiloxane trimer, the effect of water, or other inhibitors, was minimal due to exclusion by the crystal lattice.

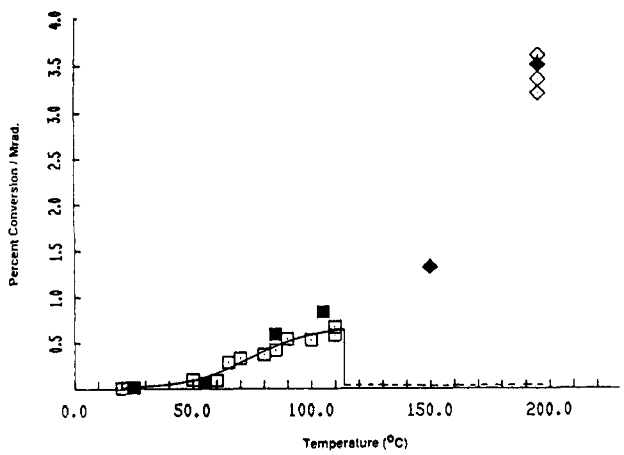


Figure 1. Radiation polymerization of hexachlorocyclotriphosphazene: ⊡, Caglioti et al.;[16] ■, superdried monomer (this work); ♦, bulk polymer in melt (this work); □, polymer in 10% decalin (this work).

Table I
Hexachlorocyclotriphosphazene Polymerization in Bulk[a]

sample no.	sublimatn times	dried over BaO times	T, °C	conversn (wt %/Mrad)
1	3	1	150	0.2
2	4	1	150	0.67
3	5	1	150	1.3
4	6	1	150	0.2
5	3	1	175	0.06
6	3	1	185	0.07
7	1	0	195	1.6
8	2	1	195	2.2
9	3	1	195	3.5
10	3	2	195	0.8
11	3	1[b]	195	1
12	3	1[c]	195	0
13	4	2	195	1.4
14	4	2[b]	195	0
15	5	2	195	0.3

[a] Dose rate 0.1 Mrad/h. [b] Recrystallized twice. [c] Recrystallized three times.

The radiation-induced polymerization in the bulk melt was very sensitive to the method and degree of purification and drying. Some typical results are given in Table I. The highest values obtained were 3.5%/Mrad or 0.35%/h, at 0.1 Mrad/h, at 195 °C. The yields were sharply dependent on temperature, and, up to 200 °C the corresponding thermal controls gave no polymer. Even at 185 °C the conversion to polymer was greatly reduced as shown also in Table I. The problem of irreproducibility, which became greater at lower temperatures, is clearly illustrated with these results. It can be comfortably assumed that the highest values are the most correct ones.[25] After more than 40 experiments in the melt it was decided that the lack of reproducibility was too severe to enable systematic studies to be undertaken and the work was continued in solution. Also the molecular weights of the polymers were always quite low with intrinsic viscosities of only about 0.2 dL/g, with the corresponding fluoroethoxy polymer, in tetrahydrofuran solution.

Some initial results, in decalin solution and conducted in separate tubes, are presented in Table II. It is clear that the condition of preparation, purification, and drying have a profound effect on the yield of polymer. Considering first the 195 °C results the first three runs were made by using the original sample of trimer. Without treatment a yield of 0.2%/h was obtained, and the corresponding thermal control gave zero yield. With decalin saturated with water a yield of 0.2%/h was also found but the thermal control contributed 0.1%/h. With 0.05% excess water added the yield was 1.0%/h, but the thermal control gave 0.88%/h. The latter two runs also gave cross-linked polymer in every case.

Table II
Influence of HCP and Decalin Purity
(Dose Rate–0.1 Mrad/h)

sample no.	dried over BaO (times)	recryst (times)	[M] mol L	temp, °C	conversn, wt %/h
1[a]	0	0	2	195	0.2
2[b]	0	0	2.1	195	0.2[d]
3[c]	0	0	2.1	195	1.0[d,e]
4	1	1	3.7	195	0.20
5	1	1	4.6	195	0.20
6	1	3	4.4	195	0.22
7	2	2	3.7	195	0.11
8	2	2	4.9	195	0.12
9	2	2	4.0	195	0.13
10	1	2	4.3	195	0.34
11	1	2	4.5	195	0.32
12	1	2	4.4	195	0.36
16	1	1	3.1	185	0.07
17	1	1	4.1	185	0.06
18	1	1	2.4	185	0.05

[a] Trimer and decalin were used as received. [b] Decalin was saturated with water. [c] 0.05% of water was added in decalin. [d] Thermal control gave 0.1%/h of conversion for sample 2 and 0.88%/h for sample 3. In all other cases there were 0% conversion with the thermal control. [e] Cross-linked products were obtained with the radiation and the thermal control samples (samples 2 and 3).

Experiments were then conducted, again at 195 °C, in which the trimer was recrystallized and dried over BaO under various conditions. It was found that one recrystallization and one BaO drying gave 0.20%/h of polymer. Three recrystallizations plus one BaO cycle gave 0.22%/h, and two recrystallizations plus two BaO cycles gave 0.11–0.13%/h. Finally two recrystallizations plus one BaO drying cycle gave 0.32–0.36/h. These were not only the highest values but also had reasonable reproducibility and were the conditions adopted for all subsequent runs. It should be pointed out again that with radiation induced cationic polymerization the highest yields are considered to be the more correct.[25] In all cases the thermal controls, even after 100 h, gave zero polymer. At temperatures below 195 °C lower yields were always found; see Table I, for example, samples 16–18.

A number of experiments were conducted by using NMR tubes and re-irradiating each time. No post-effect was observed, and this method of measuring the yields was adopted. This method had also been found to be very effective with cyclic dimethylsiloxane polymerization.[21]

Two typical conversion–time curves are presented in Figure 2. The reproducibility was quite good and well within the range of those found in the careful work of Lee, Chu, et al.[26,27] with thermal initiation using Raman and laser light scattering. The variations from run to run were attributed to the high sensitivity of the system to impurities and to small amounts of water. The latter problem is compounded with radiation-induced cationic polymerizations since these are, themselves, extremely sensitive to traces of water.

Effect of the Monomer Concentration. The internal order of the conversion–time curves fit a 3/2 power dependence of the rate on the monomer concentration. This is illustrated, for example, in Figure 3. It should be pointed out, however, that at the less than 25% conversions studied the data also fitted first-order plots. The separate tube experimental results are given in Figure 4. These give a scattered dependence of about 1.7 power. A 3/2 order would be expected if the monomer (trimer) also participates, as is firmly believed, in the initiation process.[28,29]

Molecular Weights. A number of the polymerization products were converted to the (trifluoroethoxy)polyphosphazenes and their intrinsic viscosities determined. They were all found to be about 0.2 dL/g, similar to the bulk products. The low values are probably due to chain transfer to monomer, i.e.

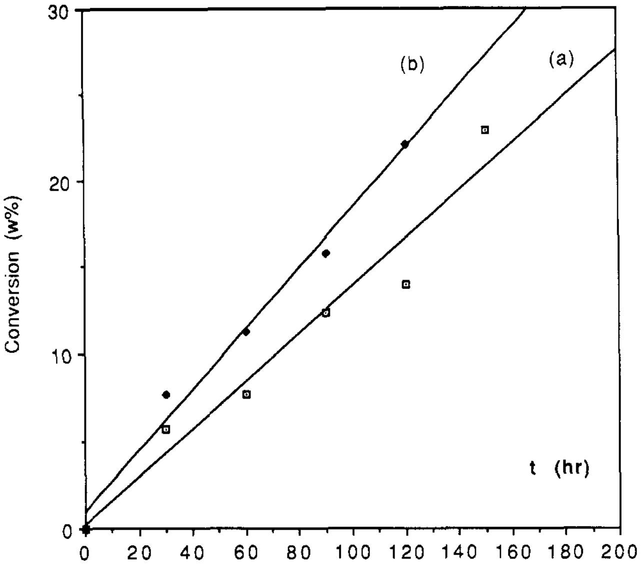


Figure 2. Radiation polymerization of hexachlorocyclotriphosphazene [HCP] in decalin: (a) [HCP] = 2.1 mol/L; (b) [HCP] = 2.4 mol/L (T = 195 °C; dose rate = 0.1 Mrad/h).

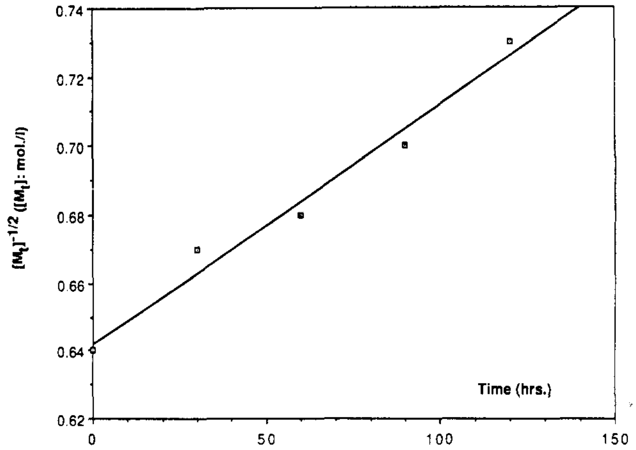


Figure 3. Radiation polymerization of HCP at 195 °C ($[M]_0$ = 2.4 mol/L; solvent, decalin; dose rate = 0.1 Mrad/h).

$$M_n^+ + MCl \rightarrow M^+ + M_nCl$$

The HCP trimer has six chlorines per monomer unit, and transfer could be very much favored over chain growth leading to the low molecular weights observed.

It is clear that the radiation approach does yield low molecular weight polymer both in bulk and in decalin solution. The rather low rates are probably the results of the low dose rates used. With high dose rates such as can be obtained with an electron accelerator practically acceptable rates should result.

Effect of Adding an Electron Acceptor. The high reactivity of the free, unpaired, cations undoubtedly leads to extensive chain transfer and rapid termination of the growing chains. It was considered, therefore, that the addition of a bulky efficient electron acceptor would introduce some ion pair and/or reduced rates of termination of the polymerization and transfer reactions. This had been tried without success many years ago with styrene and isobutylene.[30] More recently, however, Hayashi et al.[31,32] had obtained excellent results with α-methylsty-

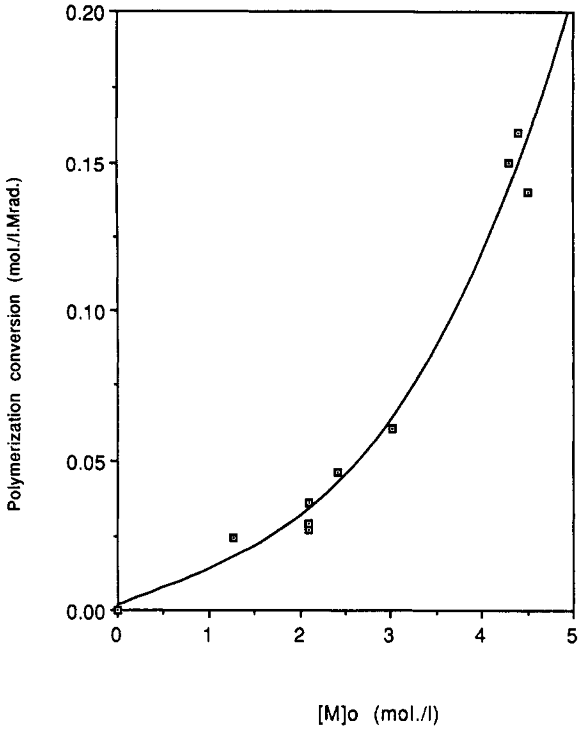
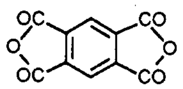


Figure 4. Influence of monomer concentration on the reaction rate (solvent, decalin; T = 195 °C; t = 60 h; dose rate = 0.1 Mrad/h).

rene and pyromellitic dianhydride. This acceptor



has now been tried with hexachlorocyclotriphosphazene in bulk and in decalin solution. In bulk no effect on the rate was obtained, but the intrinsic viscosity of the corresponding trifluoroethoxyl polymer increased from 0.2 to 0.4. These results are included in Table III. In decalin solution the results were rather remarkable and are presented in Table III. The conversion at 195 °C increased from 0.36 to 2.25%/hour with the addition of a small amount of pyromellitic dianhydride. Even at 175 °C the conversion, in the presence of the electron acceptor, increased from about 0.02 to 0.27%/h.

The temperature dependence is presented as an Arrhenius plot in Figure 5. The activation energy is about 43 kcal/mol compared with literature values of 42–57 kcal/mol reported for the thermal polymerization[33–35] and 36 ± 4 kcal/mol for the BCl_3-catalyzed polymerization.[36] The somewhat lower values found in this and the BCl_3 work presumably reflect the lower activation energies for the initiation step. The energy needed to open the conjugated trimer rings is reflected in the high overall activation energies.

Table III
Polymerization of Hexachlorocyclotriphosphazene in the Presence of PMDA in Bulk and in Decalin Solution

[M], mol/L	[PMDA],[a] mol/L	T,[b] °C	t, h	conversn, wt %/h	intrinsic viscosity, dL/g
5.75 (bulk)	0	195	60	0.35	0.2
5.75 (bulk)	0.5	195	68	0.3	0.4
4.4	0	195	61	0.36	0.2
3	0.14	195	8	2.25	0.6
2.8	0.14	185	22	0.86	
3	0.13	155	68	0.03	
3	4.5×10^{-2}	175	56	0.27	
5.75[c] (bulk)	0.18	195	50	0.56	

[a] This indicates only the quantity of PMDA introduced as it is only partly soluble under these conditions. [b] Thermal control gave zero yield at these temperatures. [c] Crude monomer without any purification.

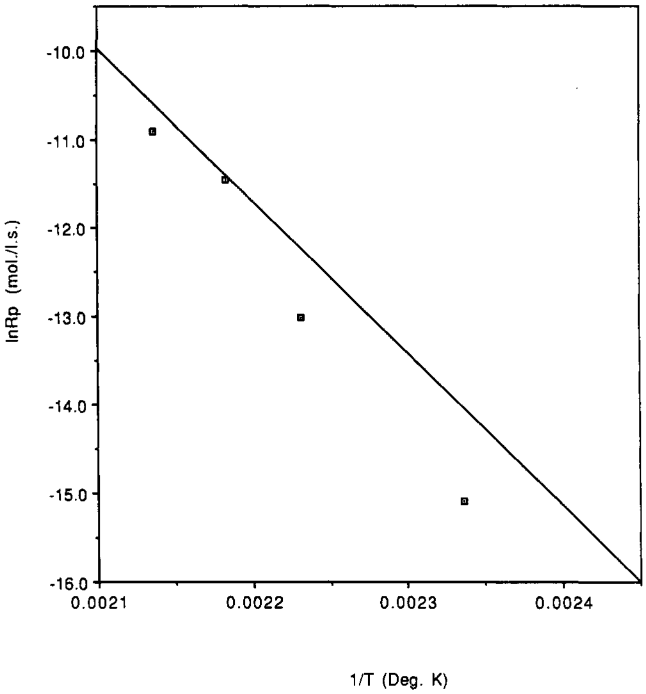


Figure 5. Solution polymerization of hexachlorocyclotriphosphazene in decalin in presence of pyromellitic dianhydride (PMDA): Dependence of Rp on temperature; [PMDA] = 0.14 mol/L; $[M]_0$ = 3 mol/L.

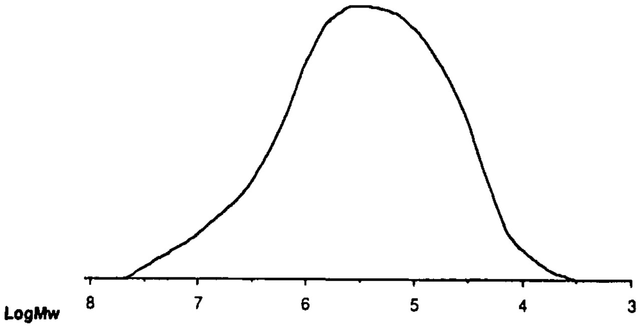


Figure 6. GPC chromatogram of (trifluoroethoxy)polyphosphazene converted from Cl polymer (elution solvent, THF; T = 40 °C.

The intrinsic viscosity data is also of considerably interest and is included in Table III. With 0.14 M pyromellitic dianhydride present the intrinsic viscosity of the corresponding polymer increased 3-fold to 0.6. This corresponds to a weight-average molecular weight of about 500 000.[37] The GPC analysis (Figure 6) showed a unimodel distribution with a wide molecular weight distribution. The NMR analysis showed an absence of any small cyclic oligomers. The M_w/M_n value was 18.7, and the peak value was 454 000. The glass transition temperature was determined with DSC as −66 °C and a $T(1)$ at 84 °C. These are the values normally reported for the trifluoroethoxy polymer.[38,39]

The considerable effect of the electron acceptor on the polymerization could be due to an increase in the free ion yield due to a reduction in geminal recombination. Considering the magnitude of the effect and also the increase in molecular weight the explanation of Hayashi et al.[31,32] for the introduction of an ion pair mode is more attractive. This suggests for α-methylstyrene that the monomer is an electron donor D which complexes with the electron acceptor A. The complex DA can be excited by the irradiation, e.g. via energy transfer, to form an ion pair. This could now initiate the polymerization and reduce the chain-transfer step. In this work the trimer itself could play the same role as α-methylstyrene, i.e. as the donor. Schematically this can be written:

$$\mathrm{D} + \mathrm{A} \rightleftarrows \mathrm{(CA)\ complex}$$

$$\mathrm{D} \rightsquigarrow \mathrm{D}^*$$

$$\mathrm{D}^* + \mathrm{(DA)} \rightarrow \mathrm{(DA)}^* + \mathrm{D}$$

$$\mathrm{(DA)}^* \rightarrow (\mathrm{D}^{\bullet+}\cdots\mathrm{A}^{\bullet-})\ \mathrm{ion\ pair}$$

$$(\mathrm{D}^{+}\cdots\mathrm{A}^*) + \mathrm{M} \rightarrow \mathrm{ion\ pair\ propagation}$$

GPC analysis of the polymer obtained shows only one main product with a very widely dispersed molecular weight distribution (Figure 5) which implies, perhaps, that mainly ion pairs are involved. The absence of small cycle oligomers would also tend to increase the rate since these are known to be much less reactive than the trimer and decrease the rate.[40]

Conclusions

Conducting the polymerization in decalin gives much better reproducibility than that found with the bulk melt.

The addition of pyromellitic dianhydride, a bulky and powerful electron acceptor, gives increased rates and molecular weights. This can be attributed to the introduction of ion pairs which could delay termination and transfer to monomer.

Although the rates are still low, increasing the dose rate should bring them up to more practical values.

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Registry No. PMDA, 89-32-7; Phosnic 390, 940-71-6; decalin, 91-17-8.

References and Notes

(1) Allcock, H. R. *ACS Symp. Ser.* **1988**, *No. 360*, 250.
(2) Singler, R. E.; Sennett, M. S.; Willingham, R. A. *ACS Symp. Ser.* **1988**, *No. 360*, 268.
(3) Singler, R. E.; Hagnauer, G. L.; Sicka, R. S. *ACS Symp. Ser.* **1987**, *No. 260*. 143.
(4) Tate, D. P.; Antowiak, T. A. *Kirk-Othmer Encycl. Chem. Technol. 3rd Ed.* **1980**, *10*, 939.
(5) Neilson, R. H.; Wisian-Neilson, P. *Chem. Rev.* **1988**, *88*, 541.
(6) Nelioui, M.; DeJaeger, R.; Puskaric, E.; Heubel, J. *Makromol. Chem.* **1982**, *183*, 1137.
(7) Allcock, H. R.; Kugel, R. L. *J. Am. Chem. Soc.* **1965**, *87*, 4216.
(8) Allcock, H. R.; Kugel, R. L.; Valan, K. J. *Inorg. Chem.* **1966**, *5*, 1709.
(9) Allcock, H. R.; Kugel, R. L. *Inorg. Chem.* **1966**, *5*, 1716.
(10) Allcock, H. R. *Phosphorus-Nitrogen Compounds*; Academic Press: New York and London, 1972.
(11) Hagnauer, G. L. *J. Macromol. Sci., Chem.* **1981**, *A16*, 385.
(12) Singler, R. E.; Hagnauer, G. L.; Sicka, R. W. *ACS Symp. Ser.* **1982**, *No. 193*.
(13) Sennett, M. S.; Hagnauer, G. L.; Singler, R. E.; Davies, G. *Macromolecules* **1986**, *19*, 959.
(14) Fieldhouse, J. W.; Fenske, S. L. U.S. Patent 4327064, 1982.
(15) Ganapathiappan, S.; Dhathathreyan, K. S.; Krishnamurthy, S. S. *Macromolecules* **1987**, *20*, 1501.
(16) Caglioti, V.; Cordish, D.; Mele, A. *Nature (London)* **1962**, *195*, 491.
(17) Cordischi, D.; Site, A. Dell; Mele, A.; Porta, P. *J. Macromol. Chem.* **1966**, *1*, 219.
(18) Burlant, W.; Taylor, C. *J. Polym. Sci.* **1959**, *42*, 547.
(19) Chawla, A. S.; St. Pierre, L. E. *J. Appl. Polym. Sci.* **1972**, *16*, 1887.
(20) Leburn, J. J.; Deffieux, A.; Sigwalt, P.; Wang, A.; Stannett, V. *Radiat. Phys. Chem.* **1984**, *24*, 239.
(21) Naylor, D. M.; Stannett, V.; Deffieux, A.; Sigwalt, P. *J. Polym. Sci., Polym. Lett.* **1986**, *24*, 319 and work to be published (Naylor, D. M. Ph.D. Thesis, North Carolina State University, 1988).
(22) Gleria, M.; Audisio, G.; Daolio, S.; Traldi, P.; Vecchi, E. *Macromolecules* **1984**, *17*, 1230.
(23) Klein, J. A.; Bell, A. T.; Soong, D. S. *Macromolecules* **1987**, *20*, 782.
(24) Allcock, H. R.; Garder, J. E.; Smeltz, K. M. *Macromolecules* **1975**, *8*, 36.
(25) Taylor, R. B.; Williams, F. *J. Am. Chem. Soc.* **1969**, *91*, 3728.
(26) Lee, D.; Ford, J. R.; Fytas, G.; Chu, B.; Hagnauer, G. L. *Macromolecules* **1986**, *19*, 1586.
(27) Chu, B.; Lee, D.-C. *Macromolecules* **1986**, *19*, 1592.
(28) Williams, F. *Fundamental Processes in Radiation Chemistry*; Ausloos, P., Ed.; Interscience: New York, 1968.
(29) Stannett, V.; Silverman, J. *ACS Symp. Ser.* **1987**, *No. 212*, 435.
(30) Stannett, V.; Bahstetter, F. C.; Meyer, J. A.; Szwarc, M. *Int. J. Appl. Radiat. Isot.* **1964**, *15*, 747.
(31) Hayashi, K.; Irie, M.; Yamamoto, Y. *J. Polym. Sci., Polym. Symp.* **1976**, *56*, 173.
(32) Yamamoto, Y.; Morinaka, A.; Irie, M.; Hayashi, K. *Macromolecules* **1977**, *10*, 266.
(33) Patat, F.; Frombling, K. *Monatsh. Chem.* **1955**, *86*, 718.
(34) Chakrabartty, D.; Ghosh, B. N. *J. Polym. Sci.* **1962**, *62*, 5130.
(35) MacCallum, J. R.; Werninck, A. *J. Polym. Sci., Polym. Chem. Ed.* **1967**, *5*, 3061.
(36) Sennett, M. S.; Hagnauer, G. L.; Singler, R. E.; Davies, G. *Macromolecules* **1986**, *19*, 959.
(37) Allen, G. *Br. Polym. J.* **1969**, *1*, 168.
(38) Allcock, H. R.; Kugel, R. L.; Valan, K. *Inorg. Chem.* **1966**, *5*, 1709.
(39) Masuko, T.; Simeone, R. L.; Magill, J. H.; Plazek, D. J. *Macromolecules* **1984**, *17*, 2857.
(40) Allcock, H. R. *Phosphorus-Nitrogen Compounds*; Academic Press: New York and London, 1972; p 319.