

γ -Radiation-Induced Telomerization of Vinyl Acetate, Styrene, and Methyl Methacrylate

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Synopsis

Vinyl acetate (VAc), styrene (St), and methyl methacrylate (MMA) were irradiated in dilute solution at an absorbed dose rate of 0.5 Mrad/hr in the absence of oxygen at room temperature. In homogeneous systems, telomers are formed with a rate $\propto [M]^1$ at monomer concentrations $[M] > \text{ca. } 0.4M$. The chain length $(\overline{D.P.}_n)$ increases with increasing $[M]$. $(\overline{D.P.}_n)^{-1}$ depends over large ranges of $[M]$ linearly on the ratio $[S]/[M]$ ($S = \text{solvent}$) in accordance with the Mayo equation. These findings were obtained with VAc in methanol and with St in cyclohexane. In heterogeneous systems, telomer is formed at all monomer concentrations. The 100-eV yield for telomer formation passes a maximum of $G_T(-M) = 40$ (MMA in 2-propanol) and $G_T(-M) = 27$ (MMA in cyclohexane) at the onset of polymer formation ($[M] \approx 3 \text{ vol-}\%$). With the system St/2-propanol, $G_T(-M) \approx 15$ was found being independent of $[M]$. The molecular weight \overline{M}_n (telomer) increased from ca. 600 to ca. 1200 by increasing $[M]$ up to 100 vol-% (MMA/2-propanol). \overline{M}_n (telomer) does not depend on $[M]$ in the other two cases ($\overline{M}_n \approx 500$, MMA/cyclohexane; $\overline{M}_n \approx 700$, St/2-propanol).

INTRODUCTION

As has been indicated recently in the book by Starks,¹ the field of telomerization is expected to grow because of the increasing use of telomers for various purposes such as plasticizers, lubricants, surfactants, etc. Many telomerization processes are based on free-radical mechanisms. High-energy radiation is an appropriate tool to initiate telomerizations since upon irradiation with γ -ray, electron beams, etc., organic substances form free radicals which are generally reactive toward unsaturated monomers. Although various researchers were concerned with the application of high-energy radiation to telomerization,²⁻⁶ it appears that only certain aspects were looked at carefully, especially those concerning the γ -ray-initiated telomerization of ethylene.³⁻⁶ The telomerization of other monomers has been investigated only occasionally.

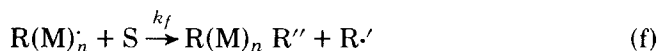
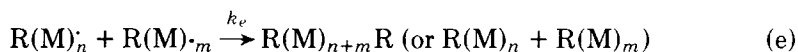
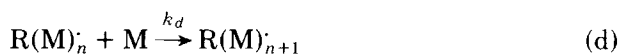
Telomerization in Solution

Generally, there are two modes of polymerizing unsaturated compounds in solution depending on whether the polymer formed is soluble in the reaction mixture or not. The experimental results described below pertain to both types of systems: (a) homogeneous systems, where the macromolecules generated during the reaction remain soluble and have to be separated after the experiment from the reaction mixture (e.g., by the addition of a precipitant); (b) heterogeneous systems, where the macromolecules are insoluble in the reaction mixture and separate automatically by precipitation. Prior to the description of experimental results, some general points shall be discussed concerning the for-

mation of telomers in reaction systems which are considered homogeneous or heterogeneous with respect to the solubility of the polymer formed by the reaction of a certain monomer.

Homogeneous Systems

If a monomer-solvent system is considered that remains homogenous during the reaction, the elementary reactions shown below will occur during the irradiation of the monomers in dilute solutions:



The degree of polymerization is given by eq. (1):

$$\overline{D.P.}_n = \frac{k_d[M]}{k_e[R(M)_n\cdot] + k_f[S] + k_g[R\cdot]} \quad (1)$$

With respect to telomer formation, two cases are of interest:

(i) The rate of reaction (f) is high. If $k_f[S] \gg k_e[R(M)_n\cdot] + k_g[R\cdot]$, the degree of polymerization $\overline{D.P.}_n$ is determined by the ratio $k_d[M]/k_f[S]$. The formation of telomers can then be achieved by any kind of radical initiation including irradiating the system with high-energy radiation by choosing an appropriate concentration ratio. Concerning the rate of telomerization, it is important whether the solvent acts as a telogen, i.e., whether the radicals $R'\cdot$ formed during reaction (f) are capable of initiating the telomerization in analogy to reactions (b) and (c).

(ii) The rate of reaction (f) is low. In this case, telomers are formed only at low monomer concentrations. Another mode of telomer formation derives from

the possibility of working at high stationary concentrations of free radicals. Such a situation can be achieved by irradiating the solution at very high absorbed dose rates, i.e., by using electron accelerators. In various cases it has been found, however, that polymers with rather high molecular weight were formed upon irradiating monomers at high absorbed dose rates.¹⁸⁻²⁰ These findings indicate that in certain cases radical reactions are paralleled by ionic reactions. The latter cause polymer formation and become dominant at high absorbed dose rates.

Chapiro et al.⁷ reported the simultaneous formation of telomer and polymer in the homogeneous system styrene/toluene. The portion of reaction product which could not be precipitated by methanol was considered as telomer. The telomer was not further characterized.

In this paper the telomer formation during γ -irradiation of two homogeneous systems is reported: styrene/cyclohexane and vinyl acetate/methanol.

Heterogeneous System

If the monomer is dissolved in a solvent which is a precipitant for the polymer, the polymer chains grow to a certain extent during the polymerization before they precipitate. Those growing chains which are terminated before reaching the critical size for precipitation remain in solution. The critical chain length should be determined in dilute monomer solution essentially by the interaction between solvent molecules and growing chains. Preferential solvation of growing chains by monomer molecules can play an important role in certain systems. If preferential solvation is not to be considered, the critical chain length should be only slightly or not at all dependent on monomer concentration, if the latter is rather low.

So far, much concern has been devoted to the precipitating polymeric products formed in heterogeneous systems. However, the telomeric products formed have attracted little attention. Wada et al. recently reported investigations on the heterogeneous polymerization of ethylene^{9,10} in bulk and *t*-butyl alcohol and vinyl acetate¹¹ in *n*-hexane. Also, the polymerization of methyl methacrylate¹² and of acrylamide¹³ in precipitating media was studied. In several cases, such as during the polymerization of styrene in methanol investigated by Huang et al.,¹⁴ the formations of polymer products possessing bimodal molecular weight distributions were observed. From these and other findings the coexistence of two polymerization mechanisms was inferred by taking into account the propagating chain being in different physical states, a loose one and a rigid one. The simultaneous formation of (nonprecipitating) telomers was not studied by these authors. In order to gain information concerning telomerization in heterogeneous systems, we irradiated methyl methacrylate in 2-propanol and cyclohexane and styrene in 2-propanol.

EXPERIMENTAL

Materials

Methyl methacrylate (Merck-Schuchardt, 99%), vinyl acetate (Merck-Schuchardt, 99%), and styrene (Ferak, 99%) were freed from stabilizer by washing with 10% NaOH solution and water. After drying with CaCl₂ and CaH₂, the monomers were distilled via a 1-m Vigreux column. The solvents were of p.a. quality (Merck). They were distilled via a splitting tube column prior to use.

Irradiations

Monomer solutions (usually 30 ml) were irradiated in glass ampoules in the field of a ^{60}Co γ -source at room temperature. The absorbed dose rate determined with the Fricke dosimeter was 0.5 Mrad/hr. Prior to irradiation the solutions were freed from oxygen by bubbling with purified argon for 30 min.

Treatment of Irradiated Samples

Polymer precipitated during the irradiation was filtered off. Nonreacted monomer and solvent were separated from the telomeric product by evaporation. The products were characterized by gel permeation chromatography either in toluene solution using Merckogel 2000 and 6000 or in tetrahydrofuran using Styragel columns. Despite pumping on the telomeric products for several days at a high-vacuum system, the samples still contained small portions of monomer (up to 4%). The monomer could be quantitatively determined by the GPC method. Molecular weight determinations were carried out on monomer-free telomers obtained by GPC fractionation. Number-average molecular weights were determined with a vapor pressure osmometer (Knauer).

RESULTS AND DISCUSSION

Homogeneous Systems

Vinyl Acetate in Methanol

Figure 1 shows that the conversion increases linearly with irradiation time up to relatively high conversions (60% to 80% depending on the initial monomer concentration). In all cases approximately 100% conversion of the monomer could be achieved. It was found [Fig. 2, curve (a)] that in the investigated range (0.13M to 3.3M) the total rate of monomer conversion v depended linearly on the monomer concentration ($v \propto [M]^1$). Such a dependence is expected¹ for photoinitiated or γ -radiation-induced telomerization if $[S] \gg [M]$ and termination occurs via reaction (e) according to eq. (2):

$$v = k_d[M][S]^{1/2}(KI/k_e)^{1/2} \quad (2)$$

where K designates a parameter involving the quantum yield or the 100-eV yield for generation of initiating radicals and I is the absorbed dose rate.

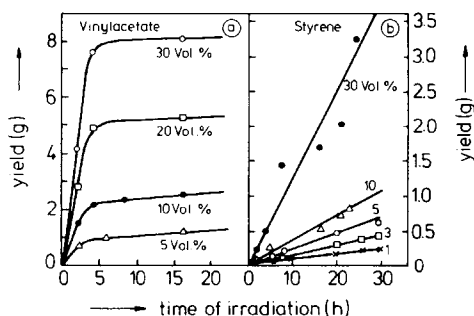


Fig. 1. Telomer yield obtained by irradiating 30-ml samples of monomer solutions as a function of irradiation time at an absorbed dose rate of 0.5 Mrad/hr and at 25°C: (a) vinyl acetate in methanol; (b) styrene in cyclohexane.

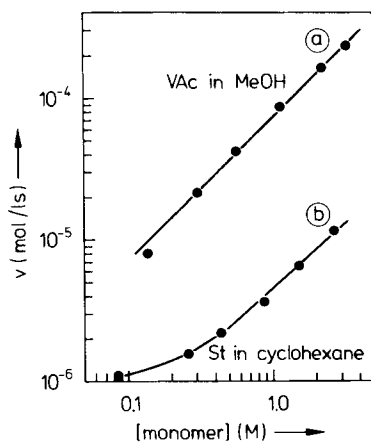


Fig. 2. Rate of telomerization vs. monomer concentration at an absorbed dose rate of 0.5 Mrad/hr and at 25°C: (a) vinyl acetate in methanol; (b) styrene in cyclohexane.

As shown in Figure 3, the reciprocal degree of polymerization increases linearly with increasing molar ratio $[\text{MeOH}]/[\text{VAc}]$ up to a value of about 50. At higher values, i.e., in more dilute solutions, $(\overline{D.P.}_n)^{-1}$ increases only weakly with $[\text{MeOH}]/[\text{VAc}]$. From the slope of the initial linear increase a transfer constant $C_s = 9 \times 10^{-4}$ was derived. C_s is defined by the Mayo equation:

$$(\overline{D.P.}_n)^{-1} = \text{const.} + C_s \frac{[\text{MeOH}]}{[\text{VAc}]} \quad (3)$$

A $C_s = 11 \times 10^{-4}$ value has been reported in the literature⁸ for the system VAc/MeOH. In that case the radical polymerization of VAc was initiated thermally by conventional initiators.

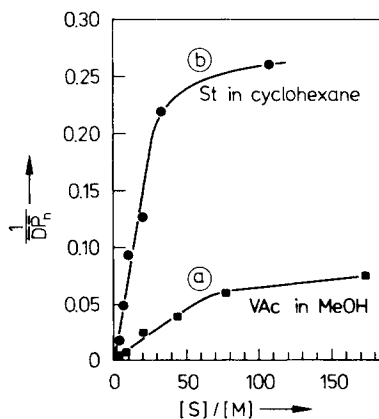


Fig. 3. Reciprocal number-average degree of polymerization as a function of the molar concentration ratio of solvent $[\text{S}]$ and monomer $[\text{M}]$ at an absorbed dose rate of 0.5 Mrad/hr and at 25°C: (a) vinyl acetate in methanol; (b) styrene in cyclohexane.

Styrene in Cyclohexane

Rates of monomer conversion v were obtained from linear plots of product yields versus time of irradiation [see Fig. 1(b)]. The double-logarithmic plot of v versus the monomer concentration exhibits a curvature at low monomer concentration, as can be seen in Figure 2, curve (b). At concentrations higher than about $0.4M$, v is proportional to $[M]^1$. Figure 3 shows that the reciprocal degree of polymerization depends linearly on the concentration ratio [cyclohexane]/[styrene] up to about a value of 30 of this ratio. At low monomer concentrations, i.e., at relatively high values of the concentration ratio, the plot bends over toward the abscissa.

The slope of the linear portion of curve (b) in Figure 3 is 6×10^{-3} , which is at variance with literature values of C_s obtained during the free-radical polymerization initiated by AIBN and other initiators: 4×10^{-6} at 60°C and 15×10^{-6} at 132°C ,^{15,16} 8.5×10^{-4} at 60°C .¹⁷

Principally, the two homogeneous systems investigated display the same behavior: at monomer concentrations above $0.3M$ to $0.4M$, the dependence of both v and $D.P._n$ on the monomer concentration is in accordance with eqs. (2) and (3).

Heterogeneous Systems*Methyl Methacrylate in 2-Propanol and Cyclohexane*

At very low monomer concentration only telomer was formed during the irradiation. Above $[M] \approx 1$ vol-% polymer precipitated. Figures 4(a) and 4(b) show the telomer and polymer yields obtained during the irradiation of 30-ml samples of solutions of MMA in 2-propanol. It can be seen that the rate of telomerization possesses a maximum at $[M] = 3$ vol-%, while the rate of polymerization is steadily increasing. Table I shows the radiation-chemical yields for telomer $G_T(-M)$ and for polymer formation $G_P(-M)$. In Table I both G values calculated on the basis of energy absorbed by the monomer and of energy absorbed by the solvent are quoted. If we assume that product formation is essentially due to the indirect effect, G values based on energy absorbed by the solvent have to be considered. Then, it can be seen that on the one hand $G_P(-M)$ is steadily increasing with increasing monomer concentration, while on the other hand $G_T(-M)$ is passing a maximum at the onset of polymer formation. At higher monomer concentration $G_T(-M)$ is leveling off. The chain

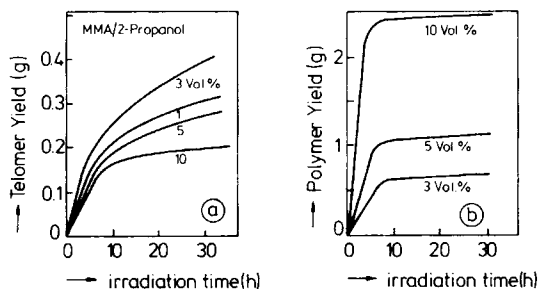


Fig. 4. Telomer yield (a) and polymer yield (b) obtained by irradiating 30-ml samples of methyl methacrylate solutions in 2-propanol at concentrations indicated at the curves, at an absorbed dose rate of 0.5 Mrad/hr and at 25°C .

TABLE I
Telomer and Polymer Yields of Heterogeneous Systems (Number of Monomer Molecules
Converted per 100 eV of Absorbed Energy)^a

System	[M], vol-%	Telomer yield		Polymer yield		\bar{M}_n (telomer)
		$G_T (-M)$	S^c	$G_P (-M)$	S^c	
MMA-2-propanol	1	2554	26	—	—	650
	3	1215	40	1943	65	850
	5	418	22	2784	149	900
	10	193	22	4793	541	1200
MMA-cyclohexane	1	1703	21	—	—	485
	3	680	27	1061	42	495
	5	263	17	2536	162	535
St-2-propanol	5	278	14	15	0.8	650
	7.5	186	15	134	11	630
	10	139	15	258	28	720

^a Absorbed dose rate: 0.5 Mrad/hr; temperature: 25°C.

^b Based on energy absorbed by the monomer.

^c Based on energy absorbed by the solvent.

length of the telomers is slightly increasing with increasing monomer concentration in the case of 2-propanol solutions. A similar behavior was found for cyclohexane solutions of MMA. However, in this case the chain length of the telomer does not depend on the monomer concentration as is shown in Table I, where also respective G values are given.

Styrene in 2-Propanol

At monomer concentrations below 4 vol-%, only telomer was formed. At higher monomer concentrations, telomer and polymer were formed simultaneously. G values are quoted in Table I. $G_T(-M)$ is independent of monomer concentration in the range investigated (up to 10 vol-%), while $G_P(-M)$ increases steadily. The chain length of the telomers does not depend on the monomer concentration.

CONCLUSIONS

In homogeneous systems, the γ -radiation-induced formation of telomers at moderate absorbed dose rates is feasible by irradiating dilute monomer solutions at room temperature in the absence of oxygen. In appropriate solvents not possessing typical telogen properties, telomers are formed with chain lengths essentially determined by the concentration ratio of solvent to monomer.

In heterogeneous systems, telomers are also formed. The simultaneous formation of polymer is not of disadvantage since the polymer precipitates and can be easily separated from the remainder of the reaction mixture. For the investigated systems the chain length of the telomers was found to be independent or only slightly dependent on monomer concentration. Thus, irradiation of heterogeneous systems appears not to be appropriate for the synthesis of telomers of variable chain length.

References

1. C. M. Starks, *Free Radical Telomerization*, Academic Press, New York and London, 1974.
2. A. A. Beer, P. A. Zagovets, and A. G. Shostenko, *Zh. Vses. Khim. Obshchest.*, **18**, 255 (1973).
3. N. P. Tarasova, A. G. Shostenko, and P. A. Zagorets, *Khim. Vys. Energ.*, **10**, 460 (1976).
4. N. P. Tarasova, P. A. Zagorets, A. G. Shostenko, A. M. Dodonov, and A. M. Oparin, *Zh. Org. Khim.*, **12**, 1879 (1976).
5. A. B. Terentev, M. A. Churilova, V. I. Dostavalova, and V. A. Svoren, *Izv. Akad. Nauk SSSR, Ser. Khim.*, **8**, 1814 (1974).
6. B. Dederichs, A. Saus, and H. P. Rath, *Erdöl Kohle*, **28**, 430 (1975).
7. A. Chapiro, P. Cordier, K. Hayashi, I. Mita, and J. Sebban-Dannon, *J. Chim. Phys.*, **56**, 447 (1959).
8. See ref. 1, p. 169.
9. T. Wada, T. Watanabe, M. Takehisa, and S. Machi, *J. Polym. Sci., Polym. Chem. Ed.*, **8**, 1585 (1974).
10. T. Watanabe, T. Wada, S. Machi, and M. Takehisa, *J. Polym. Sci. B*, **10**, 741 (1972).
11. T. Wada and S. Machi, *J. Polym. Sci. B*, **11**, 115 (1973).
12. T. Wada, M. Takehisa and S. Machi, *J. Polym. Sci., Polym. Chem. Ed.*, **12**, 1629 (1974).
13. T. Wada, H. Sekiya, and S. Machi, *J. Polym. Sci., Polym. Chem. Ed.*, **13**, 2375 (1975).
14. T. J. Beach, C. M. Burns, and R. Y. M. Huang, *J. Polym. Sci., Polym. Chem. Ed.*, **13**, 2291 (1975).
15. G. Henrici-Olivé and S. Olivé, *Adv. Polym. Sci.*, **2**, 496 (1960/1961).
16. R. A. Gregg and F. R. Mayo, *Disc. Faraday Soc.*, **2**, 328 (1947).
17. J. E. Glass and N. L. Zutty, *J. Polym. Sci. A-1*, **4**, 1223 (1966).
18. I. Sakurada, T. Okada, K. Hayashi, and J. Takezaki, Report JAERI-M 6702, 1976, p. 34.
19. D. R. Squire, J. A. Cleaveland, T. M. A. Hossain, W. Oraby, E. P. Stahel, and V. T. Stannet, *J. Appl. Polym. Sci.*, **16**, 645 (1972).
20. C. C. Allen, W. Oraby, T. M. A. Hossain, E. P. Stahel, D. R. Squire, and V. T. Stannet, *J. Appl. Polym. Sci.*, **18**, 704 (1974).

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