

This article was downloaded by:

On: 25 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

The Radiation Polymerization of 4-Methyl-1-pentene, 2-Methyl-1-butene, and 2,3-Dimethyl-1-butene under Conditions of Extreme Dryness

J. Kohler^a; A. Goineau^a; V. Stannett^a

^a Department of Chemical Engineering, North Carolina State University, Raleigh, North Carolina

To cite this Article Kohler, J. , Goineau, A. and Stannett, V.(1974) 'The Radiation Polymerization of 4-Methyl-1-pentene, 2-Methyl-1-butene, and 2,3-Dimethyl-1-butene under Conditions of Extreme Dryness', Journal of Macromolecular Science, Part A, 8: 8, 1375 – 1380

To link to this Article: DOI: 10.1080/00222337408068638

URL: <http://dx.doi.org/10.1080/00222337408068638>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

The Radiation Polymerization of 4-Methyl-1-pentene, 2-Methyl-1-butene, and 2,3-Dimethyl-1-butene under Conditions of Extreme Dryness

J. KOHLER, A. GOINEAU, and V. STANNETT

Department of Chemical Engineering
North Carolina State University
Raleigh, North Carolina 27607

ABSTRACT

The γ -ray initiated polymerization of 4-methyl-1-pentene, 2-methyl-1-butene, and 2,3-dimethyl-1-butene has been studied under conditions of extreme dryness. Only low yields of oily low molecular weight polymers were obtained. It is suggested that the low propagation rate constants are responsible for the results obtained.

INTRODUCTION

The radiation-induced polymerization of liquid isobutylene, which now seems clearly to proceed by a cationic mechanism, has led to considerable research with other vinyl monomers. Work in this field has been well reviewed by Williams [1] and by Hayashi [2]. In

general the polymerization appears to propagate by free carbonium ions rather than ion pairs and is inhibited by even minute traces of water.

It is clear that a study of other olefins under super-dry conditions would be of great interest. Kennedy, Hayashi, Okamura, and their co-workers did carry out such studies [3, 4] with 3-methyl-1-butene and 4-methyl-1-pentene. In spite of rigorous drying, only low yields of oily products were obtained under conditions where parallel experiments with isobutene gave very high yields of high-molecular-weight polymer [4]. Furthermore, the IR and NMR spectra showed the products to be those obtained by a free radical rather than the rearranged structure obtained by the carbonium ion mechanism.

In this paper the results reported for 4-methyl-1-pentene were confirmed using even more rigorous drying conditions, and two additional olefins, 2-methyl-1-butene and 2,3-dimethyl-1-butene, have also been investigated.

EXPERIMENTAL

Materials

4-methyl-1-pentene (Research Grade, purity >99.8%), 2-methyl-1-butene, (Pure Grade purity >99.5%), and 2,3-dimethyl-1-butene (Research Grade, purity >99.6%) were all obtained from the Phillips Petroleum Co.

Procedure

Three severe drying procedures were used. The particular one used in each run is reported in Tables 1 and 2 and Fig. 1.

In all cases the monomers were stored over calcium hydride for several weeks and degassed 2 or 3 times. They were then distilled over 2 to 4 sodium mirrors until no dissolution of the mirror could be seen. In some cases the monomer was then distilled over barium oxide which had been previously baked out at 400°C for several days under high vacuum. In a third procedure the monomer was distilled in a flask containing molecular sieves which had been baked out at 500°C under a vacuum of 10^{-7} Torr.

In all cases the monomers were thoroughly degassed by several freeze-thaw cycles under high vacuum and distilled directly into glass ampules which had been baked out at 500°C under 10^{-7} Torr. The tubes were then irradiated at a dose rate of 0.15 Mrad/hr in a ^{60}Co source. After irradiation the tubes were opened and the polymer isolated by drying to constant weight under vacuum. All the polymers were low-molecular-weight oily materials.

TABLE 1. Effect of Drying Method on the Radiation-Induced Polymerization of 4-Methyl-1-pentene at 30°C

Drying method	Dose (Mrads)	Yield (%)	G (Monomer)
Undried	11.1	0.94	9.7
CaH ₂ + Na + BaO	11.1	0.98	10.1
	7.6	0.71	10.7
	48.7	4.87	11.5
CaH ₂ + Na	7.5	0.71	10.8
	7.5	0.68	10.4
	48.7	6.18	14.6
CaH ₂ + molecular sieves	6.2	0.66	12.5
	6.2	0.57	10.7
	10.7	1.27	13.7
	10.7	1.28	13.9

TABLE 2. Radiation-Induced Polymerization of 2-Methyl-1-butene and 2,3-Dimethyl-1-butene

Monomer	Temperature (°C)	Drying method	Dose (Mrads)	Yield (%)	G (monomer)
2-Methyl-1-butene	30	None	30.0	1.1	5.0
	30	CaH ₂ + Na	29.6	1.1	5.1
	40	None	25.0	1.04	5.8
	40	CaH ₂ + Na	100	4.7	6.5
	-78	None	11.9	0.32	3.7
	-78	CaH ₂ + Na	11.9	0.36	4.2
	-78	CaH ₂ + Na	2.2	0.06	3.8
2,3-Dimethyl-1-butene	30	CaH ₂ + Na	2.0	~0	-
	30	CaH ₂ + Na	27.0	0.1	-
	-78	CaH ₂ + Na	25	0.1	-
	-78	CaH ₂ + Na	100	0.6	-

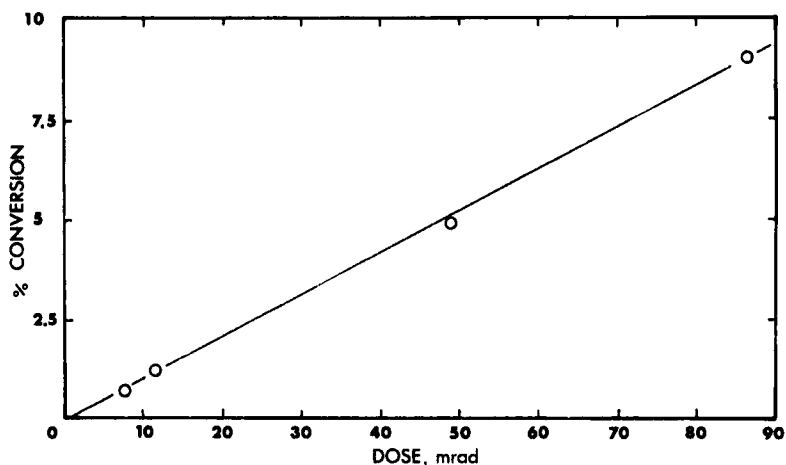


FIG. 1. The radiation-induced polymerization of 4-methyl-1-pentene at 30°C. Monomer dried over calcium hydride, sodium mirrors, and barium oxide. Dose rate: 0.16 Mrads/hr.

RESULTS

The yields were reproducible. A typical run is shown in Fig. 1 for 4-methyl-1-pentene. The method of drying appeared to have little effect on the yields within experimental error as shown in Table 1. The molecular weights were determined by vapor phase osmometry and found to vary between a \overline{DP}_n of 4.3 to 5.6. All these results are in accord with these previously published. The IR spectra were also similar to those reported by Kennedy et al. [3]. The results confirm that even under the most rigorous drying conditions only 1,2-addition to oil products, probably by a free-radical mechanism, takes place.

Two other monomers where, unlike 4-methyl-1-pentene, no rearrangement is necessary to stabilize the carbonium ions were studied. These were 2-methyl-1-butene and 2-3 dimethyl-1-butene. The results obtained are presented in Table 2; again only oily polymers were obtained. The yields were very low with both monomers, but it appeared clear that no high-molecular-weight polymer but only small yields of oily low-molecular-weight polymer were obtained, independent of the method of drying. Similar results were reported for 3-methylbutene-1 in the literature [3, 4] and by Williams [5].

DISCUSSION

The polymerization of vinyl monomers by the free-cation mechanism initiated by high-energy radiation is limited by a number of factors [1, 2]. This type of polymerization is extremely sensitive to water and other impurities. It appears that such impurities are regenerated during the polymerization process, and also that such inhibiting impurities may be generated by the radiolysis of the monomer. In addition, the carbonium ions produced from the initial molecule ion radicals and the subsequent growing chains must be sufficiently stable to allow adequate time for propagation. Finally, due to the very low stationary state concentration of the growing chains, very large propagation rate constants are necessary for measurable rates of polymerization to be obtained.

It is known from the example of isobutene that such conditions are met with this particular monomer. This is not so, however, with the other olefins studied. There seems no reason to believe that the degree of drying and purification were inadequate. Also it is difficult to conceive that terminating impurities could be produced by the radiolysis of pure hydrocarbons under strictly anhydrous and oxygen-free conditions. All the olefins studied should lead to stable carbonium ions either directly or by rearrangement. It appears, therefore, that the lack of any measureable cationic polymerization in the other olefins studied must be due to their low propagation rate constants. Although high-molecular-weight polymers have been obtained with aluminum trichloride and other Friedel-Crafts catalysts, no comparative rates of propagation for the various monomers are available. There seems little doubt, however, that isobutylene does polymerize far more readily than the other monomers concerned. 4-Methyl-1-butene, 3-methyl-1-butene, and 2,3-dimethyl-1-butene all undergo rearrangement on undergoing cationic polymerization [6, 7]. It is clear that the initial carbonium ions of the first two monomers gain considerably in energy in going from secondary to tertiary carbonium ions. This is not the case, however, with 2,3-dimethyl-1-butene, and the 3-2 hydride shift is believed to be due to steric hindrance [7]. No rearrangement, for example, takes place with the fourth monomer, 2-methyl-1-butene [7].

It is well known that even with isobutylene there is considerable steric hindrance in the polymer [8]. With the addition of an additional methylene group, it is reasonable to believe that the propagation rate constant would be considerably reduced. Presumably with the other monomer the hydride shift involved in the propagation step would also lead to a lower propagation rate. There is some evidence, for example, that considerable activation energy is involved in the 3-2 hydride shift with 2,3-dimethyl-1-butene [7].

The reduced propagation rate constants coupled with the low stationary concentration of carbonium ions, estimated to be about

10^{-10} mole/liter or the dose rate used [1], would be sufficient to explain the lack of carbonium ion polymerization. α -Olefins are notoriously inert to polymerization by free radicals, which accounts for the poor yields of low-molecular-weight oils actually obtained.

ACKNOWLEDGMENTS

We would like to thank the Division of Isotopes Development, U.S. Atomic Energy Commission for their support of this work and Professor J. P. Kennedy for very helpful discussions.

REFERENCES

- [1] F. Williams, in Fundamental Processes in Radiation Chemistry (P. Ausloos, ed.), Wiley-Interscience, New York, 1968.
- [2] K. Hayashi, in Actions Chimiques et Biologiques des Radiations, Vol. 15 (M. Haissinsky, ed.), Masson, Paris, 1971, pp. 145-183.
- [3] J. P. Kennedy, K. Ueno, L. Hayashi, and S. O. Kamura, J. Macromol. Chem., **1**, 243 (1966).
- [4] K. Ueno, A. Shinkawa, K. Hayashi, and S. Okamura, Bull. Chem. Soc. Japan, **40**, 421 (1967).
- [5] F. Williams, Private Communication.
- [6] J. P. Kennedy and A. W. Langer, Fortschr. Hochpolymer. Forsch., **3**, 508 (1964).
- [7] O. E. Van Lohuizen and K. S. De Vries, J. Polym. Sci., C, **16**, 3943 (1968).
- [8] P. J. Flory, Principles of Polymer Chemistry, Cornell Univ. Press, Ithaca, New York, 1953, pp. 246-256.

Accepted by editor May 28, 1974

Received for publication June 10, 1974