

The Irradiation of Vinyl Monomers in the Presence of Paraffin Waxes

A. C. THOMAS, T. A. DU PLESSIS, ANNE OOSTERHUIS, and
HENRIËTTE OOSTERHUIS, *Chemistry Division, Atomic Energy
Board, Pretoria, Republic of South Africa*

Synopsis

The radiation-induced grafting of a series of monomers onto a wide range of paraffin waxes was attempted. Although no grafting could be achieved and only homopolymers were formed, the rates of homopolymerization were greatly enhanced in the presence of the wax. This phenomenon is ascribed to processes of energy transfer from the irradiated wax to the monomer.

INTRODUCTION

Ionizing radiation lends itself admirably to the production of graft copolymers,¹ the process in its simplest form merely requiring irradiation of the backbone polymer in the presence of the monomer to be grafted. Much interest has therefore been shown in radiation-initiated graft copolymerizations since they are easier to handle than most conventional chemical techniques and are generally comparable as far as costs are concerned. In addition, the radiation-induced grafting methods are very general, due to the nonselective absorption of radiation in matter and can therefore be used to induce grafting of monomers onto a wide variety of substrates.

Paraffin waxes are a by-product of the petroleum industry and are relatively inexpensive and readily available materials. They are chemically very similar to polyethylene, which readily undergoes grafting reactions initiated by radiation²; and, with the aforementioned principles in mind, it was decided to attempt the grafting of various vinyl monomers onto a selection of locally available waxes by irradiation techniques in an effort to modify the character of the waxes and thus extend their capabilities as useful commodities.

EXPERIMENTAL

Table I lists the monomers and waxes used in this study. The monomers were all of chemical purity and were used as such without further purification. The reactants were degassed prior to mixing and sealing in glass ampoules. In nearly all cases, a 25% (w/w) monomer content was

TABLE I
List of Monomers and Waxes Used in the Investigation

Monomers	Waxes ^a	Congealing point, °C
1. Methyl methacrylate (MMA)	1. Sasolwaks M1	57-60
2. Acrylonitrile (ACN)	2. Sasolwaks A1	90
3. Vinylidene chloride (VDC)	3. Sasolwaks A2	97
4. Butyl acrylate (BA)	4. Sasolwaks A3	95
5. Vinyl acetate (VA)	5. Sasolwaks A4	95
6. Styrene (ST)	6. Sasolwaks A5	100
7. Ethyl vinyl ether (EVE)	7. Sasolwaks A14	83-90
8. Isobutyl vinyl ether (IBVE)	8. Sasolwaks F3	71-77
9. Trichloroethylene (TCE)	9. Sasolwaks H1	94
10. Hexachlorobutadiene (HCBd)	10. Sasolwaks L1	36-42
	11. Sasolwaks L2	44-47
	12. Waksol A	29-32

^a The waxes were kindly supplied by the Sasol Marketing Co. Ltd., Johannesburg.

used. Since the solubility of the majority of the monomers in the waxes is very low, the contents of the ampoules, after sealing, were heated to the melting point of the wax and shaken vigorously to obtain as homogeneous a distribution of monomer in the wax as possible. Control experiments were carried out to determine any polymerization produced by these procedures, but in no case was any significant polymerization detected.

The combination thus prepared was subjected to a dose of 2.5 Mrad in a ⁶⁰Co irradiating unit (Gammabeam 650, AECL) at a dose rate of 0.5 Mrad/hr. The mean temperature of a sample during irradiation was 33°C. After irradiation, the contents of the ampoules were treated by Soxhlet extraction for 24 hr to separate the wax from the homopolymer formed, after which the residues and extracts were dried to constant weight, solvent being first removed from the extracts.

RESULTS AND DISCUSSION

The extraction results showed quantitative conversion of monomer to homopolymer in the case of the first six monomers listed in Table I with each of the waxes used, indicating that no measurable degree of combination of polymer and wax occurs. Visual examination of the different portions indicated that no combination had occurred, and infrared spectra of the extracted waxes showed no bands other than those of the waxes themselves. In addition, examination of the products on a hot-stage polarizing microscope showed that the partly crystalline waxes melted at the same temperatures as the virgin waxes, leaving behind solid, noncrystalline portions, presumably aggregates of homopolymer. (All of these monomers produce noncrystalline polymers under the conditions used.) Irradiation of the waxes in the absence of monomer produced no detectable change in their molecular weights or infrared spectra.

The last four monomers listed in Table I do not polymerize readily by free-radical mechanisms and therefore do not polymerize under the action

TABLE II
The Conversion of EVE, IBVE, TCE, and HCBD To Polymer

Type of wax	Weight of reactant, g	% Monomer	Weight after γ -irradiation and heat treatment, g
EVE			
M1	8.93	43	8.90
M1	13.97	28	13.71
A2	15.97	15	15.88
A5	15.52	25	15.70
IBVE			
A1	12.98	30	12.76
A14	12.63	26	12.63
L2	12.85	25	waxy liquid
L1	12.53	24	waxy liquid
HCBD			
M1	13.17	33	13.02
A5	12.63	26	12.17
A4	12.51	27	11.96
WA	12.42	26	liquid
TCE			
A1	12.98	28	12.59
F3	13.00	29	12.42
WA	12.61	24	liquid

of gamma irradiation under normal conditions, e.g., unless super-dried,³ in which case ionic mechanisms can occur. Nevertheless, it was apparent that polymerization had occurred in each case in the presence of the various waxes. The products of these experiments were not subjected to extraction since no suitable solvents for separating wax from polymer could be found. Instead, the products were heated, after irradiation, to above the melting point of the waxes in order to evaporate any unpolymerized monomer. Table II gives some of the results obtained, and it may be clearly seen that little loss in weight occurred, indicating that a high percentage conversion to polymer had taken place except in those experiments involving the soft waxes L1, L2, and Waksol A.

The question that arises from these latter results is whether grafting of polymer to wax had occurred, or whether the wax merely acted as an initiator for the homopolymerization of these monomers. Differential scanning calorimetry (DSC) was used in an attempt to answer this question in the case of the vinyl ethers. These monomers were polymerized using FeCl_3 as initiator, and the glass transition peaks (-30°C to -35°C) of the resulting polymers were used to calibrate the instrument. The polymer/wax thermograms showed small peaks corresponding to the glass transitions of the homopolymers, and the area under these peaks corresponded closely to the amount of monomer used. DSC is not able to differentiate conclusively between a homopolymer mixture and a long-

sequence block copolymer; but, in view of the quantitative extraction results and infrared spectra obtained with the other monomers, it is also unlikely that such block copolymers occur in the case of these four monomers.

A possible explanation for the rapid homopolymerization of these monomers by radiation is that initiation is caused by radicals formed in the wax which therefore behaves in a manner comparable to that of alcohols in ethylene solution polymerization⁴ and to that of various backbone polymers in grafting reactions of styrene.^{5,6,7} In order to ascertain whether this is the case, some preirradiation experiments were carried out. Finely powdered wax was irradiated in vacuo at -196°C before adding deaerated monomer and allowing the reactants to warm slowly to room temperature. Percentage conversions of between 30 and 80 were obtained for the various monomers, showing that the wax is an important source of initiating radicals and that in the case of those monomers which do not readily form free radicals by radiolysis, it becomes the main source of initiating radicals.

Among the first six monomers in Table I, styrene is something of an exception in that, although it is readily polymerized by a free-radical mechanism using chemical initiation, it polymerizes only very slowly by radiation initiation, requiring more than 50 Mrad. It was found that in the presence of the solid waxes, complete conversion to polystyrene was observed at a dose of 2.5 Mrad. The waxes could be completely extracted from the polymer, again showing that no significant combination of wax and monomer occurs. Styrene therefore parallels the last four monomers in Table I in respect of its wax-initiated homopolymerization by gamma irradiation. In view of the fact that the radiation-induced polymerization of styrene has considerable potential applications (e.g., polymer-impregnated materials) due to its low cost in South Africa, the polymerization of this monomer in the presence of waxes is being investigated in more detail.

In conclusion, the results have shown that despite the readiness of polyethylene to undergo grafting,² a negligible degree of grafting onto the paraffin waxes is achieved, but that radicals formed in the waxes markedly enhance the homopolymerization of the monomers.

References

1. A. Chapiro, *Radiation Chemistry of Polymeric Systems*, Interscience, New York, 1962, p. 598.
2. A. Chapiro, *Radiation Chemistry of Polymeric Systems*, Interscience, New York, 1962, p. 620.
3. T. A. Du Plessis, PEL 218, Atomic Energy Board, Pretoria, 1971.
4. A. C. Thomas, *J.S. Afr. Chem. Inst.*, in press.
5. V. T. Stannett, K. Arai, J. A. Gervasi, and S. W. McLeskey, *J. Polym. Sci.*, **A3**, 3763 (1965).
6. S. Machi, I. Kamel, and J. Silverman, *J. Polym. Sci. A-1*, **8**, 3329 (1970).
7. T. Takamatsu and K. Shinohara, *J. Polym. Sci. A-1*, **4**, 197 (1966).

Received December 8, 1972

Revised January 18, 1973