

Molecular Sieves as Drying Agents for the Monomer in the Radiation-Induced Ionic Polymerization of Liquid Vinyl Monomers

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Synopsis

The factors which influence the drying of liquid vinyl monomers with molecular sieves are discussed. It is found that the best results are obtained by drying the monomer for at least 12 hr at -15°C on molecular sieves that received no pretreatment at elevated temperatures. Although the prepolymerization that takes place on the molecular sieves during the drying can be quite extensive, the excellent reproducibility that can be achieved by using this method makes it a promising drying technique.

INTRODUCTION

Due to the extremely high rates of polymerization and the resulting high molecular weights of the polymers formed, radiation-induced free-ionic polymerization has received considerable interest.¹⁻⁶ As a result of these very high rates of polymerization, however, the free-ionic polymerization process is extremely sensitive to the presence of trace amounts of inhibitors of the propagating ionic polymer chain.⁷ Most important of these inhibitors is water which can successfully inhibit the ionic polymerization process at concentrations as low as $10^{-7}M$.⁷

Elaborate drying techniques have been developed for drying the monomer and the glassware with which it comes into contact.⁸ In all these investigations it proved to be a formidable task to achieve the desired levels of dryness, and it can take many weeks to obtain a few milliliters of such a super-dry monomer.

It is obvious that such rigorous drying techniques reduce any industrial potential of these processes, and without the possible application of other drying procedures, radiation-induced ionic polymerizations can only be of limited practical importance. The utilization of surface-active drying agents such as silica gel or molecular sieves for drying large volumes of monomer to a high level of dryness seems a logical line to follow. Dried

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silica gel as a drying agent for styrene has been previously employed by Metz⁹ with promising results.

As part of an investigation of the radiation-induced polymerization of isobutyl vinyl ether in bulk and in solution, the authors used molecular sieves as the sole drying agent for the monomer.¹⁰ An empirical investigation of the major factors which influence the drying of the monomer with molecular sieves was carried out, and the results are presented in this paper.

EXPERIMENTAL

Isobutyl vinyl ether (IBVE) was obtained from Eastman Organic Chemicals and was of an industrial grade. The monomer was vacuum distilled at 25°C on a fractionating column.

Methylene chloride was obtained from Fisher Scientific Company and was of an analytical grade. This solvent was given a single distillation on a fractionating column and was used without any further treatment.

Davison molecular sieves were used for drying the monomer and were obtained from Fisher Scientific Company. Type 3A (Grade 564), 8–12 mesh sieves with an effective pore size of 3 Å were used. The decision to use these sieves was based on the low acidity of these sieves, a factor which is of prime importance to the lowering of the prepolymerization which takes place on the sieves during drying of the monomer.

The irradiations were carried out in the nominal 6 kCi ⁶⁰Co source of the Department of Chemical Engineering, North Carolina State University at Raleigh.

Sample preparation and all other experimental procedures are discussed elsewhere.¹⁰

RESULTS AND DISCUSSION

Pretreatment of Molecular Sieves

One of the major problems associated with the application of molecular sieves as a drying agent for monomers which readily undergo cationic polymerization is the polymerization of the monomer on the sieves due to their acidic nature. The choice as to which molecular sieves to use for drying the monomer was, accordingly, based on the lowest residual acidity, as supplied by the manufacturer, in order to minimize the prepolymerization on the molecular sieves.

Baking or degassing of the molecular sieves at high temperatures has a marked influence on the drying properties of these drying agents. Unfortunately, degassing of the molecular sieves at elevated temperatures not only enhances the drying efficiency, but it also increases the prepolymerization on the sieves considerably. As follows from Table I, the monomer completely polymerizes on the sieves after degassing the sieves at 500°C, as compared to a value of only 20% when the degassing is carried out at room temperature. The best results were thus obtained by not treat-

TABLE I
Influence of Treatment of Molecular Sieves on Drying Efficiency and on
Prepolymerization on the Sieves^a

Treatment	Degassing temp., °C	<i>G</i> (-monomer)	Prepolymer- ization, %
Untreated	25	185	20
Untreated	500	—	100
Washed with NaOH	25	16	0
Washed with NaOH	500	263	34
No sieves used	—	18	—

^a At 20 hr of contact time between the monomer and the sieves at 0°C.

ing the sieves at high temperatures and by carrying out all degassings at room temperature.

It further follows from Table I that the value of *G*(-monomer) as a measure of the level of dryness achieved is increased tenfold by drying the monomer with molecular sieves. A remarkable feature of molecular sieves as drying agents is the excellent reproducibility of the results that can be obtained from one batch to another. This further points to the fact that the sieves always dry the monomer to the same level of dryness. The importance of the molecular sieves as a drying agent for the monomer is thus clearly shown.

An attempt was made to reduce the prepolymerization through neutralizing the residual acid on the molecular sieves, by treating the sieves with a 0.05*N* aqueous solution of sodium hydroxide, and washing the sieves thoroughly with distilled water after the treatment, followed by drying and degassing of the sieves at room temperature. As follows from Table I, this treatment completely eliminated the prepolymerization, but the drying efficiency of the sieves was reduced to a level where the value of *G*(-monomer) was the same as that for the undried monomer. Sieves treated in a similar way were degassed for a few hours at 500°C in an attempt to increase the drying efficiency. These treated and baked sieves resulted in a value for *G*(-monomer) that was higher than that obtained for the untreated sieves. Unfortunately, however, the prepolymerization on these sieves also increased to very high levels.

Influence of Drying Temperature

As indicated in Figure 1, the conversion of the monomer to polymer at 20°C at an irradiation dose of 2.25×10^{19} eV g⁻¹, indicating the level of dryness achieved, reaches an optimum value at a drying temperature of about -15°C, in good agreement with the data supplied by the manufacturers of the sieves. As the drying temperature did not have a marked influence on the drying efficiency over the temperature range investigated, the investigation was carried out with monomer that was dried at 0°C in order to simplify the experimental procedures.

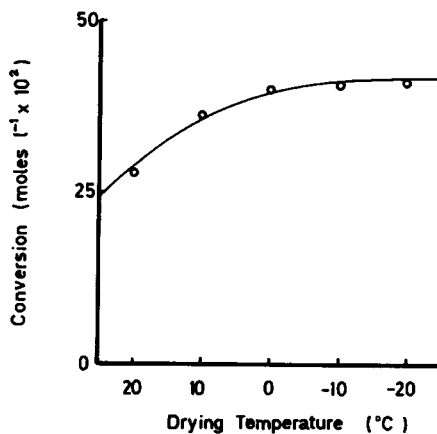


Fig. 1. Conversion of IBVE at 20°C at an irradiation dose of 2.25×10^{19} eV g⁻¹ as a function of the drying temperature of the monomer on the molecular sieves, taken at a constant drying time of 20 hr.

Influence of Time of Contact between Monomer and Molecular Sieves

The conversion of the monomer to polymer at 20°C and at an irradiation dose of 2.25×10^{19} eV g⁻¹, again indicating the level of dryness achieved, is given in Figure 2 as a function of the time of contact between the monomer and the molecular sieves at 0°C. It follows from this figure that the level of dryness reaches a constant value after about 12 hr of contact between the monomer and the sieves. This asymptotic nature of the level

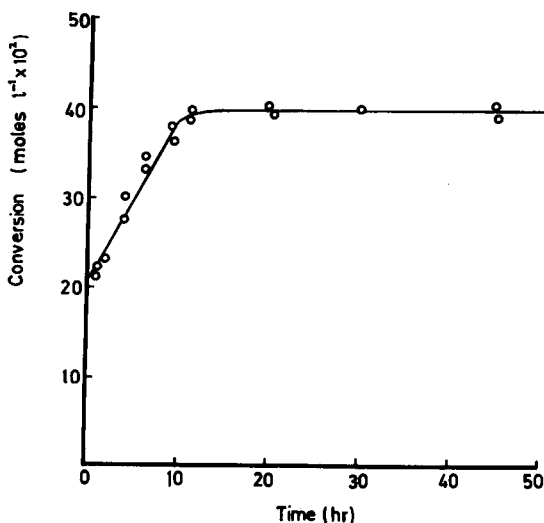


Fig. 2. Conversion of IBVE at 20°C at an irradiation dose of 2.25×10^{19} eV g⁻¹ as a function of the time of contact between the monomer and the molecular sieves as drying agent at a drying temperature of 0°C.

of dryness with contact time with the drying agent is similar to that found by Machi⁹ for drying styrene with silica gel.

This does not necessarily imply that the monomer is completely dry after 12 hr, but rather that an equilibrium is reached for drying the monomer with molecular sieves. This was further confirmed by the fact that drying the monomer for periods of more than 12 hr on three successive batches of molecular sieves did not result in an increase in the rate of polymerization.

It was furthermore observed that stirring of the monomer in contact with the molecular sieves had no effect on the drying efficiency.

Prepolymerization on the Molecular Sieves

As would be expected, the prepolymerization of the monomer that takes place on the molecular sieves is directly proportional to the time of contact between the monomer and the sieves, as follows from Figure 3.

It was further noted that the addition of methylene chloride to the monomer led to a marked enhancement of the prepolymerization if the monomer and the solvent were dried simultaneously on the same batch of molecular sieves, as indicated in Figure 3. Accordingly, the monomer and solvents were always dried separately in order to minimize the prepolymerization on the molecular sieves.

Under the optimum drying conditions, the number-average molecular weight of the polymer formed on the molecular sieves had a value of 6.7×10^4 , a relatively high value which can easily lead to erroneous results if the prepolymer is allowed to mix with the monomer to be irradiated.

From the results obtained in this investigation, it follows that molecular sieves can be used with good results to dry liquid vinyl monomers to a fairly high level of dryness. The prepolymerization on the sieves during the

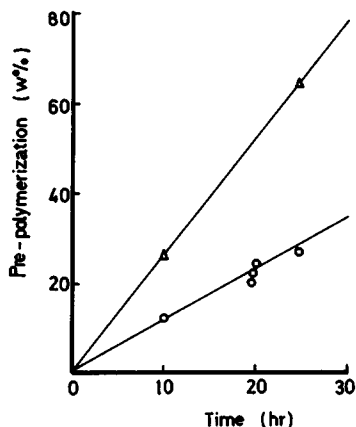


Fig. 3. Prepolymerization of IBVE on the molecular sieves at 0°C as a function of the time of contact between the monomer and the molecular sieves in the presence and absence of methylene chloride: (Δ) in presence of methylene chloride; (O) for bulk monomer.

drying might hamper its usefulness, but the good reproducibility of this drying technique makes it attractive.

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