

科研成果报告

Study on sensitized radiation polymerization of solid trioxane on pilot-scale

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Keywords: sensitized radiation polymerization solid trioxane acetic anhydride active species

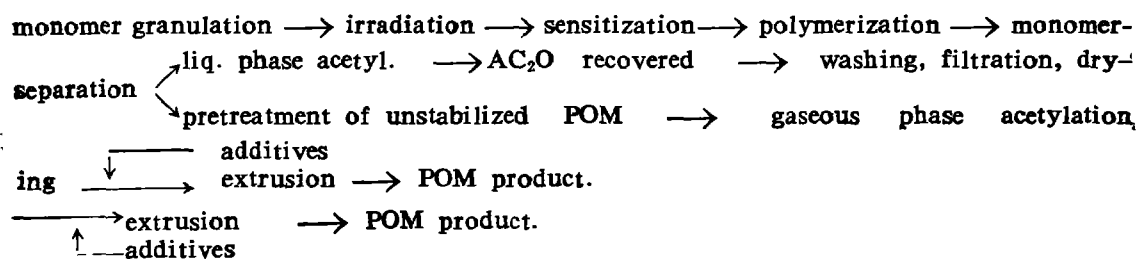
Introduction

It is well known that the rate of conversion in the process of radiation polymerization of solid trioxane generally reaches 60—70%, not exceeds 75%^[1]. Scientists engaged in this study have taken pains to find the way of increasing the rate of polymerization. For instance, by applying multi-radiation and postpolymerization, the conversion does reach 90% or even more^[2]. Unfortunately, this brings about drastic degradation of polyoxymethylene^[3]. Because of the lower conversion, a great amount of unreacted monomer has to be extracted with an enormous volume of acetone or hot deionized water, causing the consumption of an excessive amount of the solvent, of the labor and of the time.

As for sensitized radiation polymerization, a conversion of more than 90% was obtained and the output of radiation (product) was doubled at a reduced total dose of 0.5 Mrad instead of 1 Mrad for the original process. With the high conversion, the unpolymerized monomer can be removed simply by extraction under reduced pressure, which greatly simplified the operation, i.e., saving organic solvent, filtration and drying step, time and labor^[4].

The products with same quality were achieved by stabilization with acetic anhydride either in liquid or gaseous phase, while AC_2O used in the latter condition amounts only about to 1/30 of that in the former, furthermore, the criterion for the AC_2O used in the gaseous state need not to be as high as 99.5% required for use in the liquid state.

The flow chart:



* Now is in Shanghai University of Science and Technology

Experiments and determination

1. Monomer: solid trioxane particles with a size of 2—5mm, H₂O content <300ppm.
2. Sensitizer: a kind of electrophilic halogen compound adsorbed on powdered homogeneous polyoxymethylene as a sort of carrier.
3. Total dose: 5×10^3 Gy, irradiated with an electron accelerator.
4. Polymerization: at 55—58°C, 5 h.
5. Monomer separation: at 80—90°C, vacuum 80kPa(600mmHg).
6. Gas phase acetylation: carried out by Chongqing Synthetic Chemical Works.
7. Determination of physical mechanical properties: all tests were run in accordance with GB by Shengde Plastic Works.

Results and discussion

1. Effect of H₂O content in trioxane

Samples of trioxane with different H₂O content were irradiated, sensitized and polymerized. The results of conversion and intrinsic viscosity determined are listed in Table 1.

Table 1. The effect of H₂O content in trioxane (Total dose 0.5Mrad)

Run No.	H ₂ O content (ppm)	Polym. rate (%)	intrinsic viscosity [η] (dl/g)
121	321	93.8	1.28
143	243	92.3	1.69
135	172	91.3	1.53
141	41	91.7	1.49

As it is known that in conventional chemically initiated polymerization water content in trioxane should be strictly controlled, i.e., below 100ppm. Data in table 1 show polymer yield still keeps over 90% even the H₂O content is as high as 300ppm.

2. Polymer yield

Sensitized and unsensitized irradiated monomer and sensitized non-irradiated monomer were polymerized at 55°C separately and samples were taken for determining yield and intrinsic viscosity, as shown in Fig. 1 and 2.

It may be seen that the conversion of sensitized process was much higher than that for the other two with the same quality.

3. Monomer separation

The unreacted monomer can be readily eluted with acetone which can remove certain other organic impurities at the same time. However, the solvent used should be of high purity to avoid contaminating the polymer and a set of recovery installation was required.

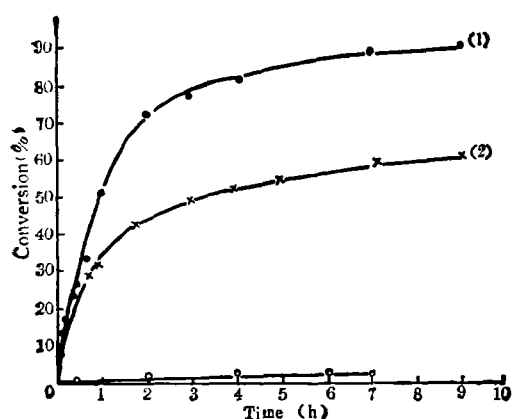


Fig. 1 The relationship between polymerization time and conversion

1. radiation sensitized
2. radiation unsensitized
3. sensitized non-radiation

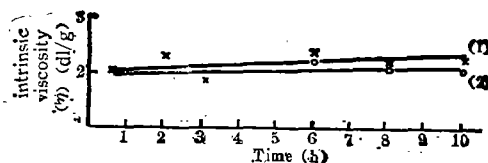


Fig. 2 The relationship between polymerization time and intrinsic viscosity

1. radiation sensitized
2. radiation unsensitized

Similar results were obtained by using hot deionized water or vacuum extraction at elevated temperature instead, as shown in Table 2.

Vacuum extraction is preferable since it was completed in a few hours, only approximately 1/5 of the time required for H₂O elution. In addition, the polymer purity from vacuum extraction is higher than that from H₂O elution.

Table 2. Comparison of methods of monomer separation

Run No.	Method of separation	Polymer yield (%)	$[\eta]$ (dl/g)	observations
161	H ₂ O elution	86.3	1.25	long term, heavy operation, large amount of energy consumption
118	ibid	90.8	2.15	
130	vacuum extraction	93.1	1.20	short period
141	ibid	91.7	1.49	simple operation, less energy
133	ibid	90.7	1.26	consumption

4. Acetylation

No appreciable difference in molecular weight or rate of thermal decomposition (K_{222}) was found in the stabilized POM from two methods as indicated in Table 3.

5. The physical mechanical properties

Polymer from radiation-sensitized polymerization was acetylated in gaseous phase and its properties were determined as:

Tensile strength (kg/cm ²)	605
Elongation (%)	40
Static flexural strength (kg/cm ²)	1040
Impact strength (kg cm/cm ²)	114
Impact strength, notched (kg cm/cm ²)	25.1
Martins test (°C)	64

Table 3. Acetylatiron results

Run No.	Methods of polymerization	[η] (dl/g)		K _{int} * (%/min.)
		Before acetylation	After acetylation	
2007	Radiation sensitized	1.56	1.60	0.069
2003		1.54	1.41	0.091
20018	Radiation unsensitized	2.26	1.92	0.08
20019		2.15	2.04	0.096

* Under atmosphere

Brief summary

In comparing with ordinary radiation polymerization, this process is found to have some merits as follows:

	Radiation sensitized process	Radiation process
1. Total dose absorbed	0.5 Mrad	1 Mrad
2. Polymer yield	90%	60—70%
3. Monomer separation	Vacuum extraction: 1) No solvent used, no impurities introduced in. 2) Simple, short period operation, low consumption.	H ₂ O elution: 1) Heavy, long term operation. 2) High consumption of solvent and energy.
4. Stabilization	1) Small amount of AC ₂ O used. 2) Purity of 98% AC ₂ O is satisfactory. 3) No AC ₂ O recovery installation required.	1) Amount of AC ₂ O needed is about 8 times of polymer. (V/W) 2) 99.5% AC ₂ O demanded. 3) AC ₂ O recovery installation needed.

References

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Abstracts in English

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A conversion rate of more than 90% was obtained in sensitized polymerization, and the output of radiation was double at a reduced total dose of 0.5 Mrad as compared to original 1 Mrad.

The unpolymerized monomer could be removed simply by extraction under reduced pressure to save a large volume of organic solvent. The quota of raw material consumption would be reduced without influencing quality of the product.

experiments indicated that the content of water in trioxane, even up to 300 ppm, has no effect on conversion or molecular weight. Irradiated trioxane was stored in dry air kept away from light at room temperature could effectively sustain the lifetime of active species even after a lapse of one month.

The infrared spectrum, molecular weight distribution and physical mechanical properties of the product from sensitized radiation polymerization were identical with those of the unsensitized process.

Keywords: sensitized radiation polymerization solid trioxane acetic anhydride
active species

A high pressure xenon-filled multiwire proportional chamber

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A high pressure xenon-filled multiwire proportional chamber is described. It can be used as balloon-borne hard X-ray telescope or hard X-ray detector in other nuclear techniques over the energy range of 10 to 200 keV.

It has a sensitive area of 700 cm² with a filling gas of 95% Xe + 5% CH₄ at 3 atmospheres pressure. Its energy resolution (FWHM) for single anode is 10% for 59.5 keV (²⁴¹Am radiation source) and 19% for 29.8 keV (the escape peak of 59.5 keV photons in xenon), and it becomes 17% and 20% respectively if all anodes are connected together. It can keep good energy resolution for three months after each gas purification.

Keywords: X-ray multiwire proportional chamber xenon high pressure