

PECULIARITIES OF PROPYLENE OXIDE COPOLYMERIZATION WITH SUPERCRITICAL CARBON DIOXIDE

**E. E. Said-Galiyev, T. V. Rakhimov, A. R. Khokhlov, V. V. Il'in*, Z. N. Nysenko*,
A. M. Sakharov***

Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,
ul. Vavilova 28, Moscow, 119991 Russia, thor@ineos.ac.ru

*N.D.Zelinsky Institute of Organic Chemistry, Leninsky prospect 47,
117913 Moscow, Russia

INTRODUCTION

Propylene oxide (PO) and carbon dioxide give a polymer involving the regular alternating copolymer poly(propylene carbonate) (PPC) [1]. PPC has many attractive features. It is formed from inexpensive and readily renewable sources, and its physical properties [2] would allow it to be processed as films with a potential utility as a biodegradable packaging material (selective permeability for oxygen) [3] and biocompatible polymer [4].

Many researchers are looking for the most effective catalyst for copolymerization alkylene oxides and CO₂. Several heterogeneous catalyst systems are known to effect this copolymerization [5], along with a homogeneous system derived from ZnEt₂/pyrogallol and an aluminum porphyrin system described by Kuran [6] and Inoue [7]. Today, there are articles devoted to solving this problem and it seems some success has been achieved [8, 9]. The influence of appropriate solvents used for copolymerization on final properties of PPC must be also studied because of cost efficiency and other reasons. The conventional approach consists of using organic solvents as polymerization media because of their good dissolving power, but related environmental disadvantages have arisen. The recent developments in the field of the supercritical copolymerization allows to compare both approaches.

In this paper, we report on the synthesis and characterization of PPC obtained from an organic medium and supercritical (SC) CO₂ (sc-CO₂) supported by the heterogeneous catalyst, zinc adipate.

I. MATERIALS AND METHODS

Materials. Propylene oxide with a purity of 99.5% was purified by distillation over calcium hydride. The as-treated PO was then stored over calcium hydride prior to use. Zinc adipate (ZnAd) was synthesized with using the known technique [9] and was dried 40 hrs at 130°C (2 Torr). We used CO₂ of high purity (>99.997%; GOST State Standard 8050-85, Russia) as received. Solvents were purified by distillation.

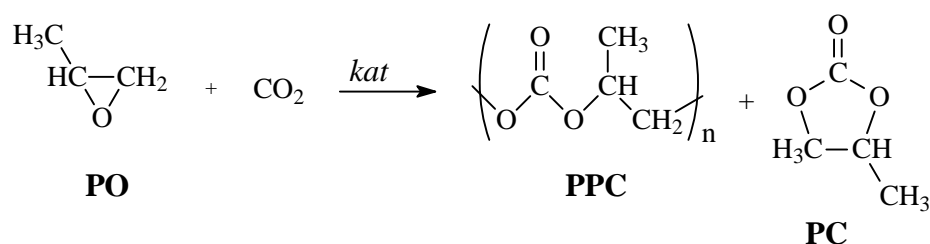
Copolymerization. The copolymerization of CO₂ and PO was carried out in 200 mL autoclave equipped with a mechanical stirrer or a 10 mL autoclave equipped with a magnetic stirrer. Dry zinc adipate (and organic medium in case non-SC synthesis) was introduced into the autoclave. Zinc adipate was treated at 70°C and 300 bar during 3 hrs before the synthesis in sc-CO₂ [10]. The autoclave was then sealed, and the entire assembly was connected through a set of capillaries to a hand pressure generator, which could provide pressure up to 600 bar. The autoclave was then pressurized. The setup included valves, heaters, and sensors for monitoring the parameters of a reaction medium. The copolymerization was performed at predetermined time and at predetermined temperature. After completion of polymerization

autoclave was cooled up to room temperature and the pressure was released. The resulting mixture was taken out, dissolved in chloroform, and treated by dilute hydrochloric acid (5%), followed by washing three times with distilled water. Finally, PPC copolymer was precipitated by pouring the concentrated copolymer solution into vigorously stirred methanol. PPC was filtered and dried for 2 days at room temperature under vacuum. Meanwhile, the resulting filtrate was distilled to remove methanol and chloroform to yield a methanol-soluble product.

II. RESULTS AND DISCUSSION

Copolymerization.

The reaction scheme is depicted as follows,



The mechanism for this copolymerization is proposed to be an anionic coordination one.

To study the effect of CO₂ concentration on the copolymerization of propylene oxide and CO₂, the process was carried out at 70 °C within 6.5 hs. The process was found to proceed with a quantitative yield of the copolymer up to the CO₂: propylene oxide molar ratio equal to 5 : 1. Extrapolation of the copolymer yield versus CO₂: propylene oxide molar ratio curve to the abscissa axis allowed us to determine the concentration of CO₂ at which the growth of polymer macromolecules virtually ceases (Fig. 1).

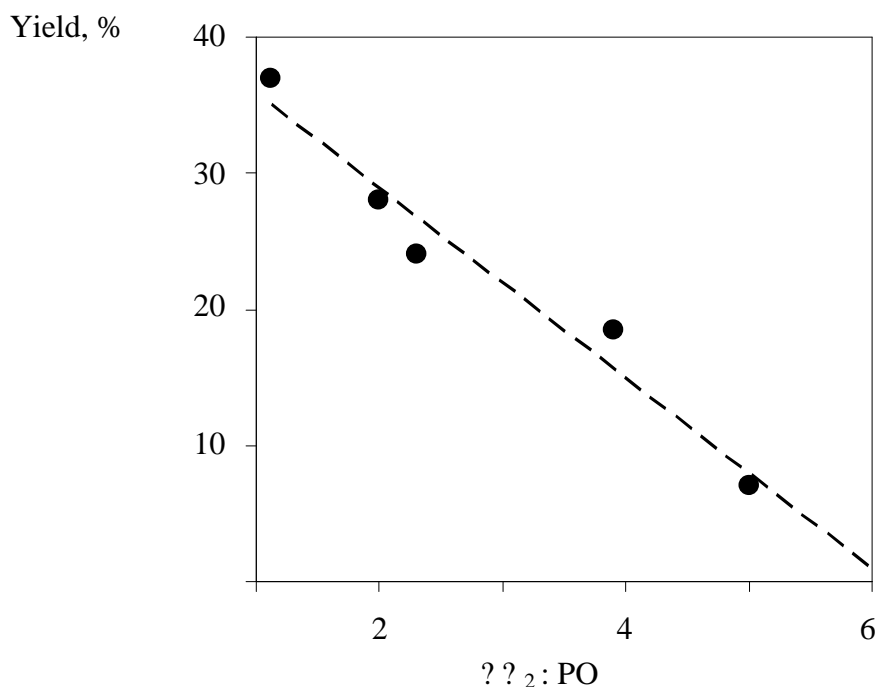


Figure 1. Plots of the polymer yield depending on molar ratio of monomers.

The yields of PPC at the different temperatures are presented in Table 1 (the best results are demonstrated only). The high yield of PPC in sc-CO₂ can be obtained at molar PO/CO₂ ratio is equal 1. A lower content of propylene carbonate (PC) in reaction mixture for sc-CO₂ was registered. Also the obtained PPC had a narrow molecular weight distribution (2.5-3.5 vs. 6-10 for organic medium); however, the PPC molecular weight was lower.

Table 1

T, °C	Methylene chloride, Yield, % from theoretic.	Supercritical conditions, Yield, % from theoretic.
50	36	68
60	46	74
70	48	78
80	49	76

Reaction time ~ 10 hs. Catalyst concentration – 20% w. from PO.

Influence of an organic solvent nature on the copolymerization was investigated by Sakharov, A. M. *et al* [11]. Increasing of a solvent polarity and basicity partially inhibits copolymerization. It should be noted that effectiveness of copolymerization also depends on CO₂ solubility in organic solvent. In case of using sc-CO₂, despite the propagating PPC is precipitating from the fluid, the growth of polymer chain has been continued.

Investigation of copolymerization kinetics allows to make conclusion on similarity of reaction features in both sc-CO₂ and organic solvent (See Fig. 2).

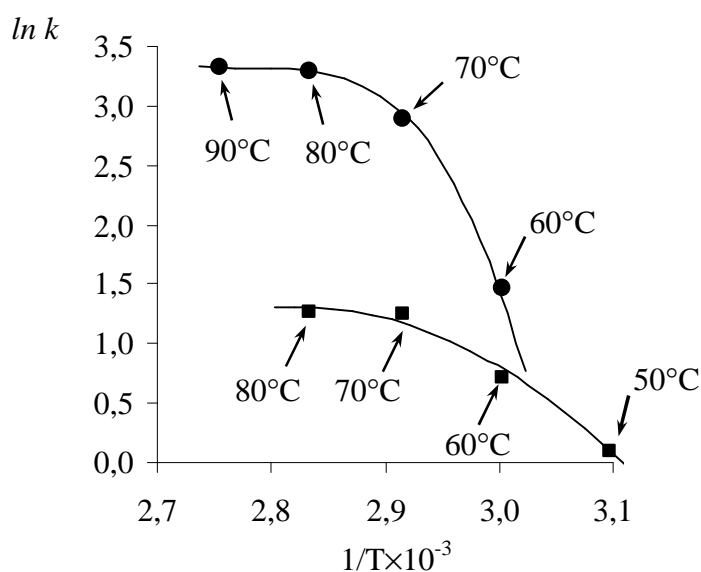


Figure 2. Dependences of $\ln k$ on the inverse temperature for: (●) – sc-CO₂ medium, (□) – the methylene chloride.

III. CONCLUSIONS

PO and CO₂ copolymerization in supercritical for CO₂ conditions leads as compared with copolymerization in organic solvent to the narrower molecular weight distribution of PPC, to the higher its yield and also to the lower PC content in reaction system. Molecular weight of PPC obtained in organic solvent is higher as a rule then that obtained in sc-CO₂. The

difference in final properties of PPC obtained by both methods is considered to be minimal. Nevertheless both mentioned approaches have their advantages. Using organic solvents for the synthesis of PPC results to an environment contamination. From the other hand sc-CO₂ technology is always more difficult for adaptation in industry. However, this technology is important for a research of a PPC formation chemical mechanism

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