

# Gel Permeation Chromatography Study of Active Centers in Propylene Oxide Polymerization Catalyzed by $C_3H_5O_3K_3$ , $C_3H_5O_3K_3-CaSO_4$ , $C_3H_5O_3K_3$ -Crown Ether, and $C_3H_5O_3K_3-CaSO_4$ -Crown Ether Systems

Mei Huang, Linxian Feng, Gengyuan Hu

Faculty of Chemical and Material Engineering, Zhejiang University, Hangzhou 310027, People's Republic of China

Received 1 June 2001; accepted 16 April 2002

**ABSTRACT:** Gel permeation chromatography (GPC) is widely used to measure the molecular weights of linear polymers. A detailed analysis of high-quality GPC data is an important source of information about the kinetics of a polymerization reaction. The living polymerization of epoxide demonstrates that the Poisson function is suitable for a molecular weight distribution description of polyether produced with catalysts containing a single type of active center. Therefore, poly(propylene oxide)s obtained by different catalytic systems, including  $C_3H_5O_3K_3$ ,  $C_3H_5O_3K_3-CaSO_4$ ,  $C_3H_5O_3K_3$ -crown ether, and  $C_3H_5O_3K_3-CaSO_4$ -crown ether, were characterized by GPC. The peaks obtained by GPC were resolved with a multi-Poisson distribution function. This signifies that there might be multiple active sites

instead of single site in these catalytic systems. The addition of calcium sulfate to the catalytic systems not only increased the molecular weight of the polyether but also effected the formation of the active sites. Furthermore, the polymerization of propylene oxide was processed in the presence of the aforementioned catalytic systems. Much useful information concerning the kinetic process of the polymerization was obtained from the GPC data with computer analysis. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 87: 2100–2105, 2003

**Key words:** catalysts; molecular weight distribution/molar mass distribution; kinetics (polym.); gel permeation chromatography (GPC)

## INTRODUCTION

Gel permeation chromatography (GPC) is widely used to measure the molecular weights (MWs) and molecular weight distributions (MWDs) of polymers. Generally, a high-quality GPC curve contains detailed information on a polymer's MWD. Many approaches have been developed that provide the means to extract detailed MWD information from GPC data.<sup>1–4</sup> Their results show that a detailed GPC analysis can be used as an important tool in kinetic studies of polymerization.

Although the polymerization of propylene oxide can be carried out with different catalyst systems, few kinetic analyses of the polymerization have been made. In this study, poly(propylene oxide) (PPO)s obtained with different catalyst systems, including  $C_3H_5O_3K_3$ ,  $C_3H_5O_3K_3-CaSO_4$ ,  $C_3H_5O_3K_3$ -crown ether, and  $C_3H_5O_3K_3-CaSO_4$ -crown ether, were characterized by GPC. Detailed information on the kinetic process of the polymerization was extracted from the data with computer analysis. On the basis of polymer GPC curves resolved by a multi-Poisson distribution function, it was found that multiple

active sites coexisted in these catalytic systems. For each catalyst system, changes in the active sites were different over the entire polymerization process, although the relative MWs of their Poisson components were almost the same.

## EXPERIMENTAL

### Materials

All reagents were reagent-grade and were purified by a conventional method. After 10 h of refluxing over calcium hydride, the propylene oxide middle cut was used for polymerization.

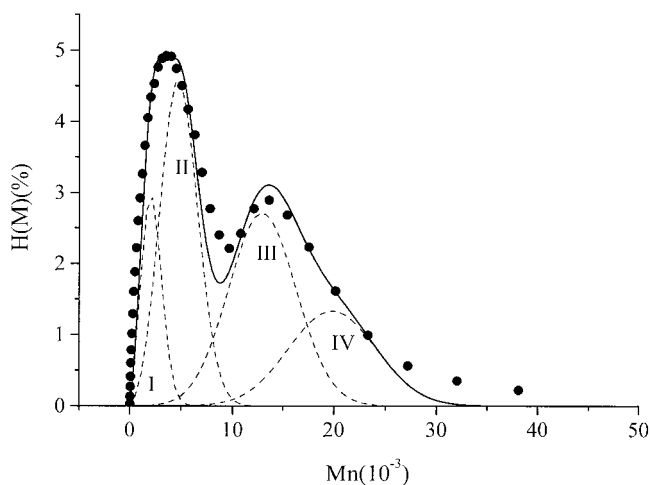
### Preparation of the catalyst

Potassium glycerine was synthesized by the reaction of potassium hydroxide with an equivalent amount of glycerine in the presence of toluene. The mixture was redistilled for 6 h. Then, the cosolvents were distilled. Finally, potassium glycerine was dried in vacuo and was used as one component of the catalyst system.

### Polymerization of propylene oxide

The polymerization reactions catalyzed by  $C_3H_5O_3K_3$ ,  $C_3H_5O_3K_3-CaSO_4$ ,  $C_3H_5O_3K_3$ -crown ether, and

Correspondence to: M. Huang.



**Figure 1** GPC data (curves) for PPO produced by potassium glyceryl. The solid circles represent original GPC data, and the dashed lines represent the data resolved with four Poisson components. The concentration ratio of the catalyst to propylene oxide was 1/400;  $M_n$  is the number-average molecular weight.

$C_3H_5O_3K_3-CaSO_4$ -crown ether were carried out in a 0.5-L stainless steel autoclave equipped with a pressure regulator and a variable-speed stirrer. The reactor was filled with 100 mL of toluene and prescribed amounts of the catalysts. Then, propylene oxide was added to the reactor. Afterward, the reactor temperature was raised to a certain value, and a polymerization reaction continued for about 6 h at a constant temperature. During the polymerization process, three samples were selected: (1) when the reaction system reached the highest pressure, (2) when the reaction system reached half of the highest pressure, and (3) when there was no change in the pressure. When the system pressure remained constant, the reaction was stopped, the polymer was taken from the autoclave, and the solvent was removed under reduced pressure.

### Analytical procedure

GPC chromatograms of propylene oxide polymers were made at room temperature on a Waters 150C gel

**TABLE I**  
Poisson Components in PPO Prepared  
by Potassium Glyceryl

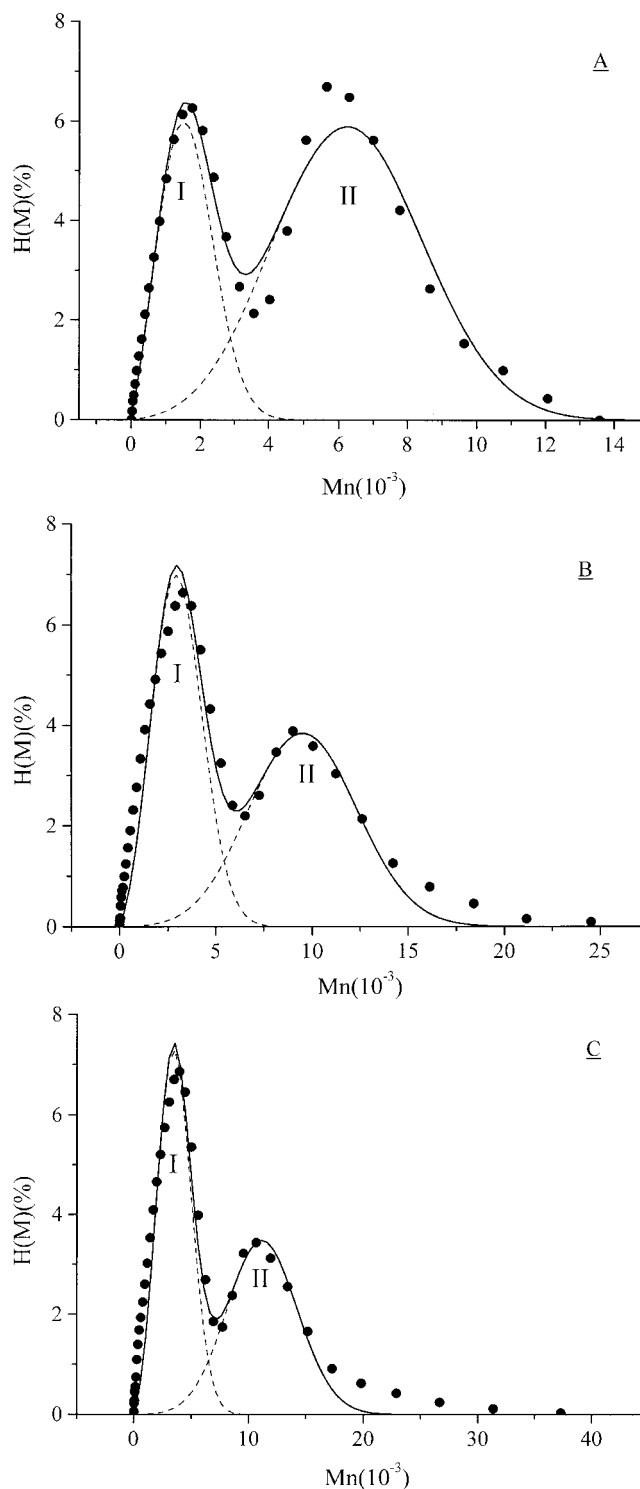
	Parameters of Poisson distribution				$M_n^a$	$M_w/M_n$
	I	II	III	IV		
K	1.385 <sup>b</sup> /11 <sup>c</sup>	3.904/32	12.01/35	18.96/22	2.214	2.85

$M_n$  = number-average molecular weight;  $M_w$  = weight-average molecular weight.

<sup>a</sup>  $M_n$  of the whole polymer by GPC in  $10^3$  g/mol.

<sup>b</sup>  $M_n$  of Poisson components in  $10^3$  g/mol.

<sup>c</sup> Fraction of the component, (wt %).



**Figure 2** GPC data (curves) for PPO produced by potassium glyceryl and calcium sulfate: (A) a sample at the point of the highest pressure, (B) a sample at the point of half of the highest pressure, and (C) a sample at the end of polymerization. The solid circles represent original GPC data, and the dashed lines represent the data resolved with two Poisson components. The concentration ratio of the catalyst to propylene oxide was 1/400;  $M_n$  is the number-average molecular weight.

**TABLE II**  
Poisson Components in PPO Prepared by Potassium Glyceryl and Calcium Sulfate

Point	Parameters of Poisson distribution		$M_n^a$	$M_w/M_n$
	I	II		
A	0.9068 <sup>b</sup> /25 <sup>c</sup>	5.380/75	1.732	2.43
B	2.182/45	8.606/55	1.947	2.56
C	2.699/49	10.254/51	2.356	2.29

$M_n$  = number-average molecular weight;  $M_w$  = weight-average molecular weight.

<sup>a</sup>  $M_n$  of the whole polymer by GPC in  $10^3$  g/mol.

<sup>b</sup>  $M_n$  of Poisson components in  $10^3$  g/mol.

<sup>c</sup> Fraction of the component (wt %).

permeation chromatograph equipped with a differential refractometer detector. The eluent was tetrahydrofuran, and the flow rate was  $1.0 \text{ mL/min}^{-1}$ . The column set consisted of three Ultrastaygel columns, one linear and two with porosity ratings of 1000 and  $500 \text{ \AA}$ . A MW calibration curve was obtained with standard polystyrene. Because there was no standard material for PPO, no recalculations were performed for the MW values of the polymers with the universal calibration rule.

### THEORY

The theory of MWD in polymers has been developed over several decades, particularly with respect to radical polymerization. The two simplest MWD functions taken from the literature are the Schulz and Flory distribution functions, although in the polymerization of ethylene oxide with an anionic catalyst, the MWD function has been demonstrated to be a Poisson distribution function. Therefore, the number distribution function of poly(ethylene oxide),  $F_n(x)$ , is

$$F_n(x) = \frac{(\gamma^{x-1} e^{-\gamma})}{(x-1)!} \approx \frac{(\gamma^x e^{-\gamma})}{x!} \quad (1)$$

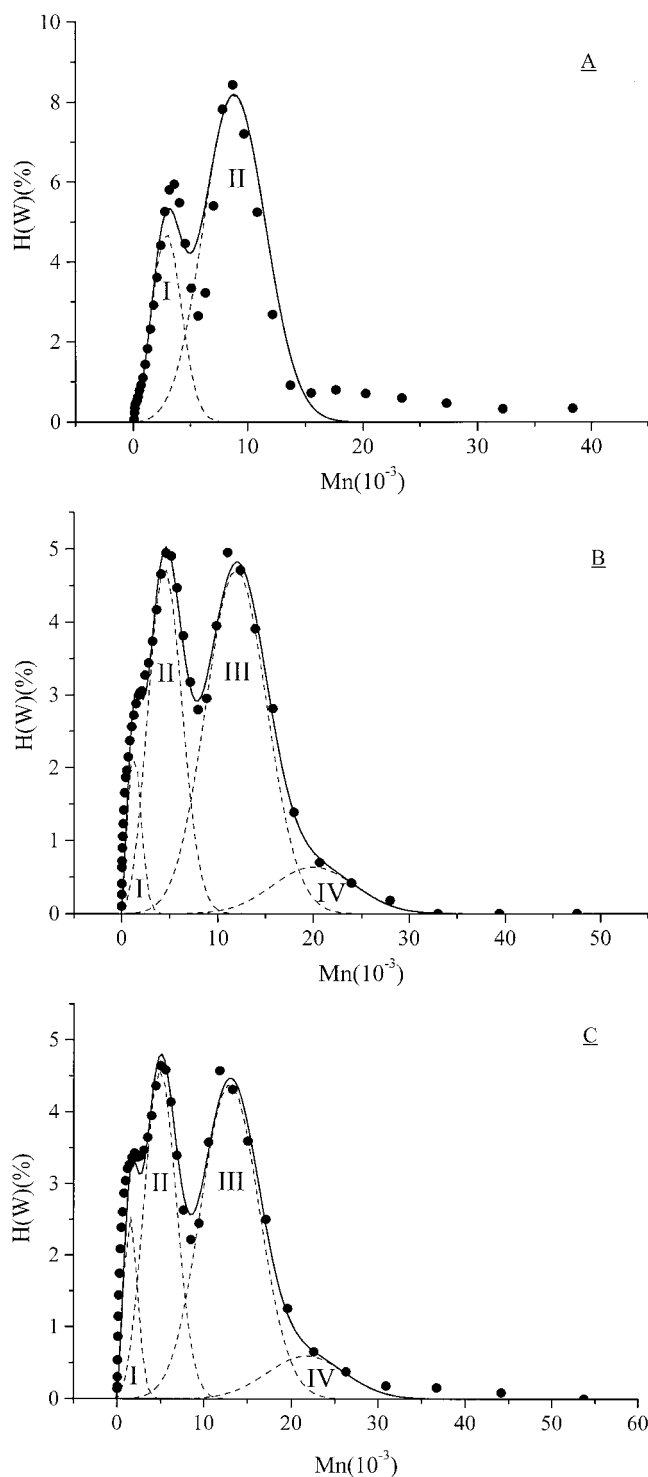
where  $\gamma$  is the average polymerization degree and  $x$  is the number of monomer units. The weight distribution function of such a polymer,  $F_w(x)$ , is given by

$$F_w(x) = \frac{\gamma^{x-1} e^{-\gamma}}{(x-1)!} \approx \frac{(\gamma^x e^{-\gamma})}{x!} \quad (2)$$

Changing it into a Gauss distribution, we obtained

$$F_w(x) = \frac{1}{\sqrt{2\pi\gamma}} e^{-\frac{x^2}{2\gamma}} \quad (3)$$

To determine the shapes of the GPC curves of polymers with  $F_w(x)$ , as described in eq. (3), one should take into account that a nearly linear correlation exists



**Figure 3** GPC data (curves) for PPO produced by potassium glyceryl-crown ether: (A) a sample at the point of the highest pressure, (B) a sample at the point of half of the highest pressure, and (C) a sample at the end of polymerization. The solid circles represent original GPC data, and the dashed lines represent the data resolved with two or four Poisson components. The concentration ratio of the catalyst to propylene oxide was 1/400;  $M_n$  is the number-average molecular weight.

TABLE III  
Poisson Components in PPO Prepared by Potassium Glyceryl and Crown Ether

Point	Parameters of Poisson distribution				$M_n^a$	$M_w/M_n$
	I	II	III	IV		
A		2.143 <sup>b</sup> /25 <sup>c</sup>	7.941/75		3.376	1.95
B	0.7088/5.0	3.679/30	11.01/55	19.06/10	2.578	2.49
C	0.9009/7.0	4.079/29	12.04/54	20.76/10	2.908	2.24

$M_n$  = number-average molecular weight;  $M_w$  = weight-average molecular weight.

<sup>a</sup>  $M_n$  of the whole polymer by GPC in  $10^3$  g/mol.

<sup>b</sup>  $M_n$  of Poisson components in  $10^3$  g/mol.

<sup>c</sup> Fraction of the component (wt %).

between the retention times,  $t$ , of the peaks of monodisperse polymers and the logarithms of their weight-average molecular weight values:

$$t = k_1 - k_2 \cdot \log(x) \quad (4)$$

The principal equation of the GPC method<sup>5</sup> correlates with  $F_w(x)$  in eq. (3) and the experimentally determined function,  $H(t)$ , which describes the height of a GPC curve as a function of  $t$ :

$$F_w(x) = H(t)[d(t)/dx] \quad (5)$$

The differentiation of eq.(4) and the substitution into eq.(5) give

$$F_w(x) = H(t)(-k_2/x) \quad (6)$$

Introducing eq. (3) for the  $F_w(x)$  function of a Poisson-distributed polymer into eq.(6), we obtained

$$H(t) \propto \frac{1}{\sqrt{2\pi\gamma}} e^{-x^2/2\gamma} \cdot x \quad (7)$$

For GPC curves of polymers with broader MWDs, combinations of several Poisson peaks with different  $\gamma$  values should be used to simulate the experimental GPC curves. The simulation equation for the computer program is given by

$$H(t) \propto \sum h_i \frac{1}{\sqrt{2\pi\gamma_i}} e^{-x^2/2\gamma_i} \cdot x \quad (8)$$

During the peak-fitting procedure, the number of the Poisson component can be subsequently adjusted to achieve a better fit of the calculated GPC curve. Because this fitting is a peak division procedure based only on experimental data, the results of the treatment determine the fewest types of most probable peaks with proper positions and intensities, the sum of which fit the experimental MWD.

## RESULTS AND DISCUSSION

The GPC method is used widely to measure MWs of linear polymers. High-quality GPC data contain detailed information on many aspects of a polymer's MWD. In the polymerization of propylene oxide, changes that happen in the polymerization process can be described with GPC analysis. Useful information is obtained from studies of polymerization kinetics.

### PPO catalyzed by $C_3H_5O_3K_3$

Figure 1 shows the GPC curves of PPO produced by  $C_3H_5O_3K_3$ . For the living polymerization of epoxide, the MWD was near 1.0, whereas for this catalyst system, the MWD became wider, and this suggests that more than one active site was present. With the Poisson distribution equation used to resolve the GPC curves of PPO, good results were obtained. They are illustrated in Figure 1, in which the solid line is the experimental GPC curve of PPO and the dashed lines were calculated for the Poisson function. The polymer produced by  $C_3H_5O_3K_3$  could be described by four Poisson distribution components with different MWs. Table I gives detailed data. From the MWD analysis, we concluded that there was more than one active site in the  $C_3H_5O_3K_3$  system.

### PPO catalyzed by $C_3H_5O_3K_3-CaSO_4$

During the polymerization of propylene oxide catalyzed by  $C_3H_5O_3K_3-CaSO_4$ , changes that happened in the polymerization process were studied. Three samples were selected for the whole reaction. The first one (A) was obtained when the system pressure reached the highest value at a constant temperature. Then, when the system pressure declined to half of the highest pressure, the second sample (B) was obtained. The third sample (C) was the final product. Figure 2 shows the GPC curves and MWD analysis for the three samples. Because the polymers catalyzed by  $C_3H_5O_3K_3-CaSO_4$  could be resolved into two Poisson compo-

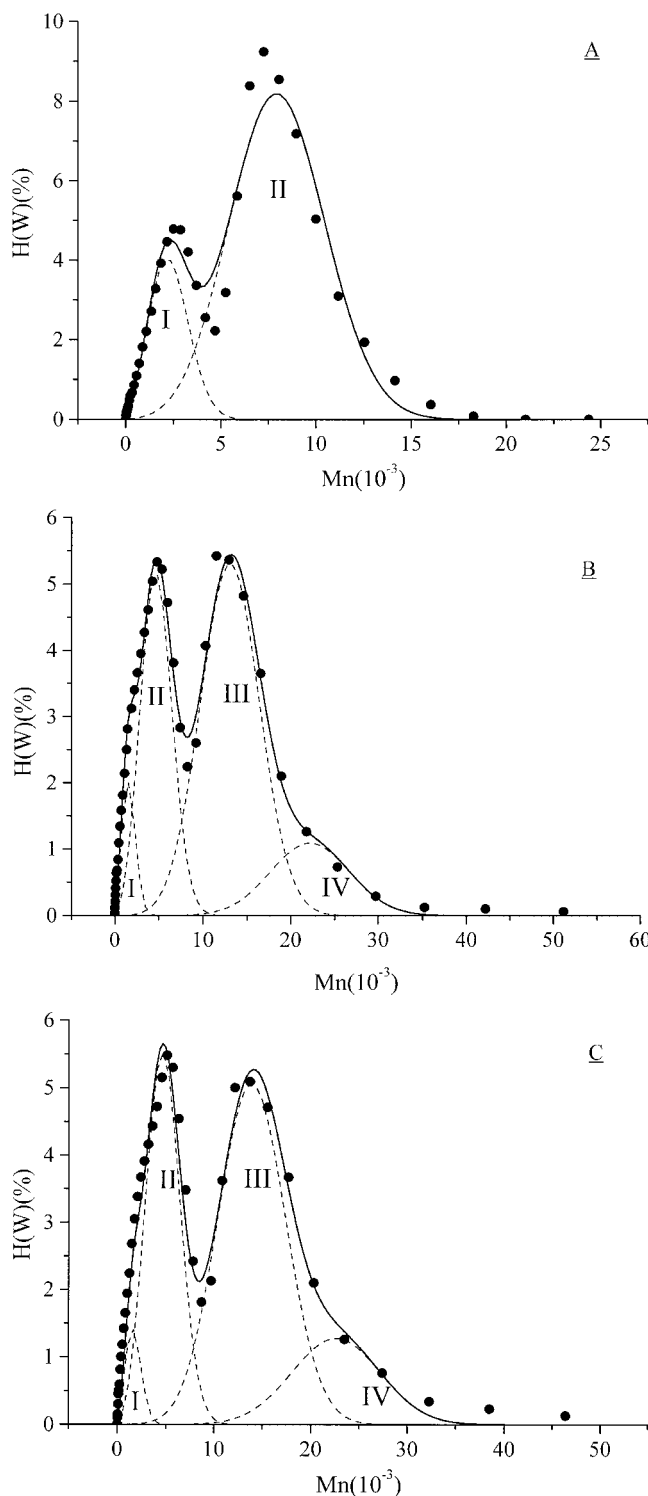
nents, there were two active sites in this catalyst system. With respect to the polymer catalyzed by  $C_3H_5O_3K_3$ , the number of active sites was reduced from 4 to 2. Therefore, the GPC analysis provided additional insight into the actual effect of the calcium sulfate on the active site in the catalyst system. It was obvious that the addition of calcium sulfate to potassium glycerine greatly affected the contributions of the lower and higher Poisson distribution components. They were so small that there were only two components in the polymers catalyzed by  $C_3H_5O_3K_3-CaSO_4$ . Therefore, the final products were obtained with higher MWs and narrower MWDs (Table II).

#### PPO catalyzed by $C_3H_5O_3K_3$ -crown ether

Polymers of propylene oxide catalyzed by  $C_3H_5O_3K_3$ -crown ether were also studied by means of a detailed analysis of GPC data (Fig. 3). Three samples (A-C) were selected in the polymerization process with the same method mentioned previously. The GPC curve of sample A was adequately described by two Poisson distribution components, whereas the GPC curves of samples B and C were fitted by four Poisson distribution components. The active sites and their corresponding contributions to each sample are listed in Table III. During the polymerization process, peaks labeled IV and I gradually emerged from the experimental data. According to a comparison of the GPC analysis of sample C with the GPC analysis of polymers catalyzed by  $C_3H_5O_3K_3$ , crown ether did not significantly change the number and MW of the Poisson component but did affect their relative fraction. Because in the  $C_3H_5O_3K_3$ -crown catalyst system the fraction of component III increased dramatically, whereas the fractions of components I and IV were much smaller, polymers were obtained with increasing MW and narrowing MWD.

#### PPO catalyzed by $C_3H_5O_3K_3-CaSO_4$ -crown ether

Figure 4 shows GPC curves of three PPO samples selected during the polymerization process catalyzed by  $C_3H_5O_3K_3-CaSO_4$ -crown ether. The way in which they were obtained was the same as that mentioned previously. The GPC curves of the polymers prepared with  $C_3H_5O_3K_3-CaSO_4$ -crown were resolved into multi-Poisson distribution components. Table IV contains the complete results of the MWD analysis. During this polymerization reaction, the changes that occurred in the active site number and its corresponding contribution were very likely the same as those that happened in the  $C_3H_5O_3K_3$ -crown catalyst system. The MWs of the Poisson component were almost the same. Therefore, with respect to the effects of crown ether and calcium sulfate, it is likely that the former



**Figure 4** GPC data (curves) for PPO produced by potassium glycerol-calcium-crown ether: (A) a sample at the point of the highest pressure, (B) a sample at the point of half of the highest pressure, and (C) a sample at the end of polymerization. The solid circles represent original GPC data, and the dashed lines represent the data resolved with two or four Poisson components. The concentration ratio of the catalyst to propylene oxide was 1/400;  $M_n$  is the number-average molecular weight.

**TABLE IV**  
**Poisson Components in PPO Prepared by Potassium Glyceryl–Calcium–Crown ether**

	Parameters of Poisson distribution				$M_n^a$	$M_w/M_n$
	I	II	III	IV		
A		1.488 <sup>b</sup> /16 <sup>c</sup>	7.038//84		2.908	2.05
B	0.9052/4	3.840/28	12.12/53	21.24/15	2.651	2.76
C	0.9537/3	3.806/28	12.95/52	21.66/17	2.872	2.65

$M_n$  = number-average molecular weight;  $M_w$  = weight-average molecular weight.

<sup>a</sup>  $M_n$  of the whole polymer by GPC in  $10^3$  g/mol.

<sup>b</sup>  $M_n$  of Poisson components in  $10^3$  g/mol.

<sup>c</sup> Fraction of the component (wt %).

played a more important role in preparing PPOs with higher MWs.

### CONCLUSIONS

A detailed analysis of high-quality GPC data is an important source of information about the kinetics of a polymerization reaction. Through the resolution of complex GPC curves into their constituents, information about distinct active species coexisting in the catalyst systems can be obtained. In our study, polymers of propylene oxide prepared with different catalyst systems, including  $C_3H_5O_3K_3$ ,  $C_3H_5O_3K_3-CaSO_4$ ,  $C_3H_5O_3K_3$ -crown ether, and  $C_3H_5O_3K_3-CaSO_4$ -crown ether, were determined by a multi-Poisson distribution function. We found not only that multiple active sites might be in these catalytic systems but also that their polymerization of propylene oxide occurred

through different process. However, it was difficult to interpret what the exact active center was. Because 18-crown-6 can complex with potassium cations, the addition of crown ether can increase the reactivity of the free alkoxide anions. Maybe free ions and ion pairs existing in the polymerization process of propylene oxide play an important part in the active center. We will continue this investigation.

### References

1. Kissin, Y. V. *Makromol Chem Macromol Symp* 1993, 66, 83.
2. Vickroy, V. V.; Schneider, H.; Abbott, R. F. *J Appl Polym Sci* 1993, 50, 551.
3. Kissin, Y. V. *J Polym Sci Part A: Polym Chem* 1995, 33, 227.
4. Aida, T.; Mizuta, R.; Yoshida, Y.; Inoue, S. *Makromol Chem* 1981, 1073, 182.
5. Yau, W. W.; Kirkland, J. J.; Bly, D. D. *Modern Size-Exclusion Liquid Chromatography*; Wiley: New York, 1979.