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Phase separation of phenolic resins

2. The fractionation of phenol-formaldehyde resin based on molecular weight and structure [a]

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Summary

The phase separation and fractionation for phenol-formaldehyde resins of the random novolak type (r-NR) were investigated by using r-NR / acetone / hexane and r-NR / acetone / cyclohexane ternary systems. The fractionation efficiency was elucidated by the partition coefficient, σ, which was derived from the theory of Flory and Huggins. The fractionation based on molecular structure and molecular weight occurred at the same time. The partition coefficient represented the fractionation efficiency based on molecular weight as well as on molecular structure.

Introduction

Phenol resin is readily prepared from phenol and formaldehyde under acidic or basic conditions. However, it is known experimentally that it is difficult to prepare fractions with narrow molecular weight distribution such as a polystyrene, effectively, because the resin has a great varieties of the degree of branch and the circumstance of methylene linkage between phenolic nuclei (*ortho-ortho', ortho-para', and para-para'*), and also the hydrogen bonds among the phenolic hydroxyl groups.

We have investigated the phase equilibrium and phase separation of phenolic resins, to elucidate the mechanism of the fractionation. In our previous paper[1], the phase separation experiments for *o*-cresol resin (*o*-CR) / acetone / cyclohexane, acetylated *o*-CR (Ac-*o*-CR)/ acetone / cyclohexane, poly(p-hydroxystyrene) (PHS) / acetone / cyclohexane, and acetylated PHS (Ac-PHS) / acetone / cyclohexane ternary systems were studied, and the effect of hydrogen bonds on the fractionation efficiency was discussed by means of the partition coefficient, σ. According to the theory of Flory[2] and Huggins[3], the coefficient σ, with which molecular species are separated between the two phases, is given by the following equation,

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a) Part 1 : cf. ref.[1]

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$$\ln\frac{V_{x(2)}}{V_{x(1)}} = \sigma X \qquad (1)$$

where X is the size parameter (in this case, the degree of polymerization), $V_{x(2)}$ and $V_{x(1)}$ are the volume fractions of species X in the polymer-rich phase and the polymer-lean phase, respectively. And,

$$\sigma = V_{p(1)}(1-\frac{1}{Xn_{(1)}}) - V_{p(2)}(1-\frac{1}{Xn_{(2)}}) + \chi\{(1-V_{p(1)})^2-(1-V_{p(2)})^2\} \qquad (2)$$

here, $V_{p(2)}$ and $V_{p(1)}$ are the total volume fraction of polymer in the polymer-rich phase and the polymer-lean phase ($V_{p(2)} = \Sigma V_{x(2)}$, $V_{p(1)} = 1 - V_{p(2)}$), Xn is the number-average of X, and χ is the polymer-solvent interaction parameter, which is assumed to be identical for all values of X.

In this paper, the phase separation experiment for phenol-formaldehyde resins of the type of random novolak, which have both molecular weight distribution and a variety of structures (degree of branches), was carried out, and the effect of molecular structure on the fractionation was discussed. In addition, the relationship between the fractionation efficiency and the molecular structure will be made clear.

Experimental

Sample preparation

Phenol-formaldehyde resin of the random novolak type (r-NR) was prepared from phenol (1 mol) and formalin (1 mol as formaldehyde) at 80 °C for 5 h, by using HCl (0.01 mol) as a catalyst. The number-average molecular weight (Mn) of r-NR was 1.2×10^3 and $Mw/Mn = 3.8$ as measured by GPC.

Phase separation

The phase separation and fractionation experiments were carried out for r-NR / acetone / hexane and r-NR / acetone / cyclohexane ternary systems at 25 ± 0.1 °C. A sample solution was stored in a glass cell sealed by silicone rubber cap with mechanical stirrer. The glass cell was immersed in a water bath at 25 °C and then a certain amount of nonsolvent was added to the glass cell by syringe. The solution was stirred for 1h and then was left for 12 h to separate into two phases. The volume of two phases was determined by measuring pipet and then the solution of the two phases was evaporated under reduced pressure to recover polymers in the two phases.

The partition coefficient, σ, was determined by the GPC method as described in the previous paper1).

Structure analysis

The molecular structure of fractionated samples in the two phases was determined by ^{1}H NMR measurement in pyridine-d_5. The *ortho* ratio (OR) was adopted as a structure parameter of the novolak, which means the reactivity ratio of the *ortho* proton to all active protons in phenolic nucleus.

$$\textit{ortho}\ \text{ratio}\ (\%) = \frac{\mathrm{I}(o-o') + \mathrm{I}(o-p')}{\mathrm{I}(o-o') + \mathrm{I}(o-p') + \mathrm{I}(p-p')} \times 100 \qquad (3)$$

where I(*o-o'*), I(*o-p'*), and I(*p-p'*) are the area of signals corresponding to *ortho-ortho'*, *ortho-para'*, and *para-para'* methylene protons between phenolic nuclei, respectively.

Measurements

GPC measurements were carried out by a Shimadzu HPLC LC-6A equipped with two TSKgel G3000HXL columns and a TOSOH UV-8011 spectrophotometer (254 nm) as detector, and THF as an eluent at 1.0 mL/min. The calibration curve was obtained by standards of phenol-formaldehyde resin with narrow molecular weight distribution ($Mw/Mn \leq 1.3$), whose number-average molecular weight was determined in acetone solution by vapor pressure osmometry (VPO). VPO was done with a Corona model 117 molecular weight apparatus. Benzil solutions were used to make the calibration curve. ^{1}H NMR spectra were recorded on a JEOL FX-100S FT-NMR spectrometer at 100 MHz. Pyridine-d_5 was used as a solvent and tetramethylsilane (TMS) was used as a reference. FT-IR spectra were obtained by a Jasco FT/IR-3 spectrophotometer with a KBr disk.

Results and Discussion

Cloud points were determined by titrating the polymer solutions with cyclohexane or hexane as nonsolvent at 25°C. Cloud points are presented in form of ternary phase diagram in Figure 1. It is found that cloud points are influenced by the precipitation ability of nonsolvent for r-NR. The precipitation ability of hexane is larger than that of cyclohexane.

The fractionation efficiency is affected significantly by the phase separation conditions, that is, the initial volume fraction of polymer, v_{p0}, and the amount of polymer partitioned in the polymer-rich phase from parent solution (the fraction size), ρ_p. Thus, when the fractionation efficiency is compared between the different systems, the phase separation conditions must be identical with each other. The relations between the partition coefficient of the first fraction and the reciprocal of X for r-NR / acetone / cyclohexane and r-NR / acetone / hexane ternary systems under the conditions, $v_{p0} = 0.050$ and $\rho_p = 0.675$, are shown in Figure 2. It is observed that the value of σ for the both systems are obviously dependent on $1/X$. This may be due to the molecular weight dependence of the polymer-solvent interaction χ[4]. In principle, a fractionation efficiency is higher as σ becomes greater[1]. The values of σ of the first fractions for r-NR / acetone / hexane system are higher than those for r-NR / acetone / cyclohexane system. The efficiency of the system using hexane as nonsolvent is higher than that of the system using cyclohexane. The precipitation ability of hexane for r-NR has been higher than that of cyclohexane as shown in Figure 1. Thus, it is found that the fractionation efficiency for r-NR is dependent on the precipitation ability of nonsolvent.

The molecular structure of polymers in the two phases was elucidated by means of ^{1}H NMR measurements. It has been known that the signals of *o-o'*, *o-p'*, and *p-p'* methylene linkage protons in ^{1}H NMR in pyridine-d_5 split into 4.3, 4.2, and 3.8 ppm, respectively[5,6]. In this study, the molecular structure of novolaks is presented by the *ortho* ratio (OR) as

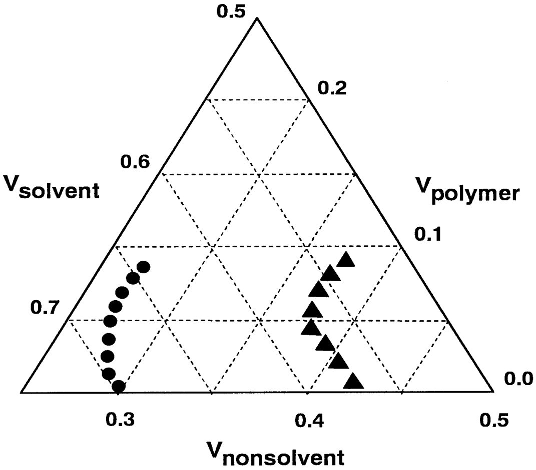

Figure 1. Ternary phase diagrams for r-NR/acetone/cyclohexane (▲) and r-NR/acetone/hexane (•) systems at 25 °C.

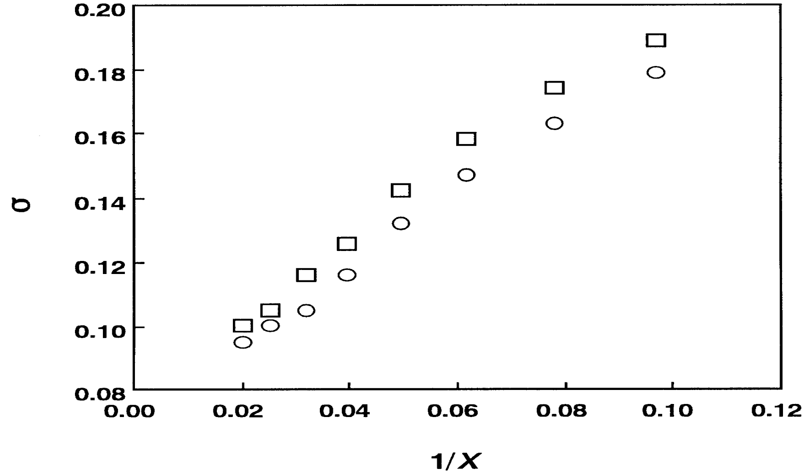

Figure 2. Plots of the partition coefficient, σ, versus the reciprocal of degree of polymerization,1/*X*: the symbols and ○ are corresponding to r-NR/acetone/hexane and r-NR/acetone/ cyclohexane ternary systems, respectively.
(V_{p0}= 0.050, ρ_p= 0.675)

shown in equation (3), which means the linearity of polymer chain. For examples, the values of OR of all-*ortho* and random novolaks are given to be 100 % and 67 %, respectively. The OR of polymers in the polymer-rich phase and the polymer-lean phase for the two systems as a function of partition coefficient σ are shown in Figure 3. In the figure, σ_{xn} is adopted as a representative value of σ, which is the value of σ at the number-average of X of the original polymer before fractionation. The validity of σ_{xn} has been confirmed by the computer simulation technique[1]. In both systems, the value of OR of polymer in the polymer-rich phase is larger than that in the polymer-lean phase. This indicates that the fractionation based on molecular structure and molecular weight occurs at the same time. And the polymer in the polymer-rich phase is more linear than that in the polymer-lean phase. A high-*ortho* novolak forms strongly intramolecular hydrogen bonds[7] so that the solubility will be poor. One can observe that the difference between the values of OR of polymer in the polymer-rich phase and that in the polymer-lean phase is larger as σ_{xn} becomes higher. This indicates that the fractionation efficiency on the base of molecular structure becomes higher with increasing σ_{xn}. The partition coefficient σ represents a fractionation efficiency on the base of molecular weight as well as on molecular structure. It is found that there is a closer relationship for random novolaks between the fractionation on the base of the molecular weight and that based on the molecular structure.

In conclusion, it was found that the fractionation for phenolic resins of the random novolak type based on molecular structure and molecular weight occurred at the same time.

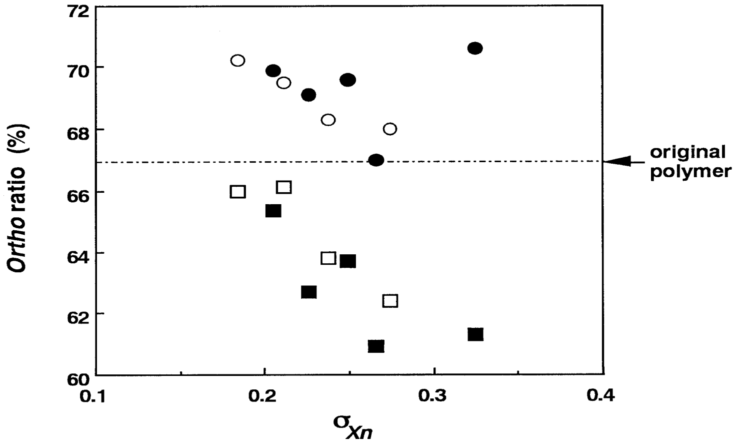

Figure 3. Plots of the *ortho* ratio versus the partition coefficient of the number-average of *X* of original polymer, σ_{Xn} : the symbols • and ■ are corresponding to polymers in polymer-rich phase and polymer-lean phase for r-NR/acetone/hexane ternary system and the symbols O and are corresponding to polymers in polymer-rich phase and polymer-lean phase for r-NR/acetone/cyclohexane ternary system, respectively.

The partition coefficient σ represented the fractionation efficiency based on molecular weight and on molecular structure, respectively. A more detailed study on the fractionation for novolaks is in progress in our laboratory.

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References

1. T. Yamagishi, J. Abe, Y. Nakamoto, S. Ishida (1992) J. Thermosetting Plastics, Jpn. **13**: 207
2. P. J. Flory (1941) J. Chem. Phys. **9**: 660
3. M. L. Huggins (1941) J. Chem. Phys. **9**: 440
4. K. Kamide, Y. Miyazaki (1981) Polym. J. **13**: 325
5. J. C. Woodberg, H. P. Higinbottom, H. M. Culbertson (1968) J. Polym. Sci., Part A, Polym. Chem. Ed. **3**: 1079
6. T. Yoshikawa, J. Kumanotani (1970) Makromol. Chem. **131**: 273
7. T. Yamagishi, M. Enoki, M. Inui, H. Furukawa, Y. Nakamoto, S. Ishida (1993) J. Polym. Sci., Part A, Polym. Chem. Ed. **31**: 675