Sorption of Benzene by Isotactic and Atactic Polystyrenes

By Hisashi Odani, Michio Kurata
and Mikio Tamura

(Received November 6, 1959)

In recent years there has been much interest in the physical properties of stereo-specific synthetic polymers. The present authors have recently studied the absorption and desorption of benzene by three isotactic polystyrenes of different degrees of crystallinity and one atactic polystyrene at 35°C[1]. Sorption isotherm data have been obtained for these systems from both integral and differential kinetic runs*.

An isotactic polystyrene (isotactic-PS) used a sample that had been prepared by stereo-specific polymerization with Ziegler's catalyst. After the purified polymer had been boiled in heptane for thirty hours, the polymer was separated into isotactic and atactic fractions, by extracting the latter with cold methyl ethyl ketone. The isotactic-PS films were obtained by the same procedure reported elsewhere[1]. The polymer films of different degrees of crystallinity were then prepared by annealing these films at three different combinations of temperature and period. These annealing conditions are summarized in Table I, in which the degree of crystallinity of each specimen estimated roughly by the X-ray method are also given. An atactic polystyrene (atactic-PS) sample used was a commercial sample, "Lustrex hi-flow 77-234", and a benzene of A. R. grade was used as penetrant. The sorption apparatus and procedure were practically the same as those reported elsewhere[1].

TABLE I. ANNEALING CONDITIONS AND DEGREES OF CRYSTALLINITY OF ISOTACTIC PS's

	Annealing condition		Degree of crystallinity
	Temp. °C	Period hr.	
Isotactic PS-I	120	2	0.08
Isotactic PS-II	180	0.5	0.45
Isotactic PS-III	160	1.5	0.50

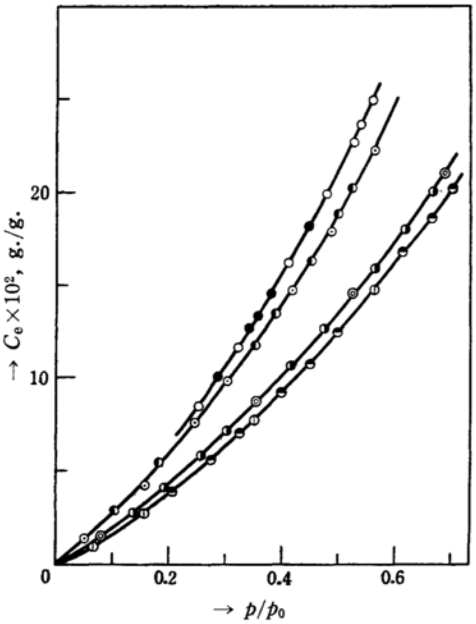

Fig. 1. Absorption isotherms of isotactic PS's and atactic PS-benzene at 35°C.

	Integral absorption	Differential absorption
Isotactic PS-I	⊙	◐
Isotactic PS-II	◎	◑
Isotactic PS-III	⦶	◒
Atactic PS	○	●

Fig. 1 gives absorption isotherms obtained for the three isotactic-PS's and for the atactic-PS at 35°C. Here the ordinate represents the mass of benzene in grams sorbed per gram of a given polymer at dry state and the abscissa the relative pressure of a given vapor in the external phase. It is seen that the isotherm in the region of medium relative pressure is much steep for atactic-PS and becomes less steep with increase of crystallinity for isotactic-PS's. This feature is analogous to that for isotherms on systems water vapor-celluloses having different degrees of crystallinity[2]. It is also seen that the data from integral absorption experiments and those from differential ones fall well on a single curve for each system.

For any given relative pressure the equilibrium amount of benzene in dry polystyrene decreases with increase in crystallinity. This suggests that benzene is mainly absorbed in amorphous regions of a given sample. If this is the case, there should hold

$$(C_e)_i=(C_e)_a(1-\phi) \qquad (1)$$

where $(C_e)_a$ and $(C_e)_i$ are the equilibrium concentrations of benzene at a given relative pressure in an atactic-PS and in an isotactic-PS in which the volume fraction of crystal region is ϕ, respectively. The values of ϕ may be calculated as a function of relative pressure by applying Eq. 1 to the data of Fig. 1. Within the range where the calculations are possible, ϕ is practically independent of p/p_0 for each isotactic-PS, giving an average value 0.10_7, 0.36_4 and 0.41_0 for the isotactic-PS-I,

---

[1] A. Kishimoto, H. Fujita, H. Odani, M. Kurata and M. Tamura, *J. Phys. Chem.*, to be published.

* The term "differential" was used to denote experiments in which the difference between initial and final pressures was sufficiently small, while the term "integral" referred to experiments in which this pressure difference was relatively large.

[2] P. H. Hermans, "Physics and Chemistry of Cellulose Fibers", Elesevier, New York (1949), Part II, Chap. II.

-II and -III, respectively. It is interesting that these values are reasonably compared to the crystallinities of respective samples shown in Table I, which were estimated from the intensities of the X-ray diffraction peaks.

The authors wish to thank Professor H. Fujita and Dr. A. Kishimoto of this University for their helpful discussions. The isotactic polystyrene sample was supplied to them by Professor J. Furukawa of this University, to whom they express sincere thanks.

Department of Industrial Chemistry
Faculty of Engineering
Kyoto University
Sakyo-ku, Kyoto