BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 44, 1145—1146(1971)

Inverse Gas Chromatographic Investigation of Fractionated Polycarbonates

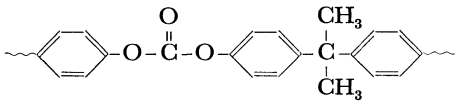
Yoshiyuki YAMAMOTO, Shin TSUGE, and Tsugio TAKEUCHI

Department of Synthetic Chemistry, Faculty of Engineering, Nagoya University, Chikusa-ku, Nagoya

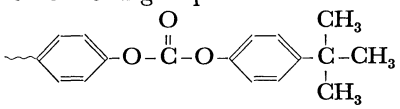
(Received August 24, 1970)

Inverse gas liquid chromatography (glc) has recently been used to measure the interactions between stationary test compounds and solute vapors. Davis, *et al.*[1] characterized asphalts by means of inverse glc. Lavoie and Guillet,[2] and Smidsrød and Guillet[3] also investigated second order transitions (*e.g.* glass transition, *Tg*) and polymer-solute interactions for polymeric materials using this method.

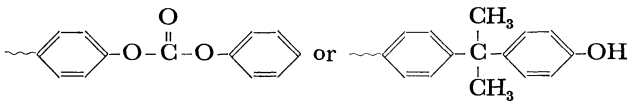
Poly[2,2-propanebis(4-phenyl carbonate)] (PC) is a most thermostable polymer and has the following repeating unit.



However, PC synthesized by the solvent method (SM-PC), in which *p-t*-butylphenol is used as terminater, provides the next end group.



On the other hand, PC synthesized by the melt method (MM-PC) is known to yield either end groups.[4]



In this work, fractionated PC with various molecular weight was investigated by means of inverse glc. Effect of the end groups, molecular weights, and *Tg* of PC on the retention behaviors are also discussed.

Results and Discussion

Molecular Weight of PC and Retention Behaviors. When polymers are used as a stationary phase in glc, it is expected that the smaller the molecular weights of the polymers, the stronger the interactions between their end groups and test solute. The interactions can also be affected by the nature of the end groups.

Figure 1 gives schematic chromatograms of benzene and diphenylmethane obtained by use of MM-PC with various molecular weights as the stationary phase in glc at 220°C. The retention time of diphenylmethane changes markedly as a function of the molecular weight of PC, while that of benzene is almost constant regardless of its molecular weight. The same tendency was observed for SM-PC.

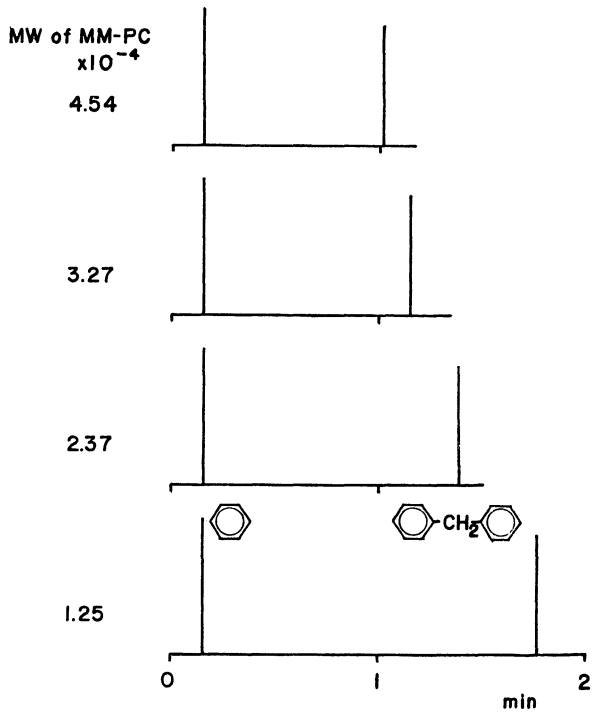


Fig. 1. Schematic chromatograms of benzene and diphenylmethane obtained by use of MM-PC with various molecular weights as the stationary phase in glc at 220°C.

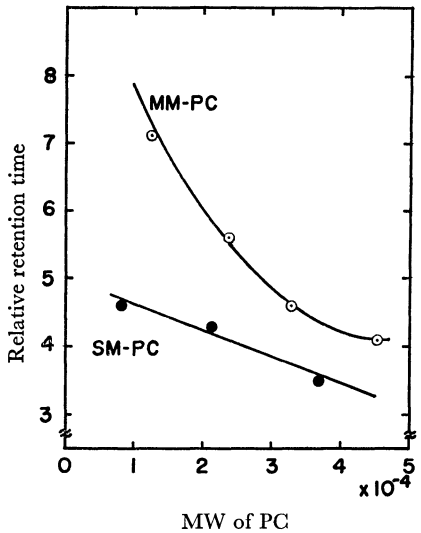


Fig. 2. The relationship between the relative retention time of diphenylmethane to benzene and the molecular weight of PC.

The results are shown in Fig. 2, where the relative retention time of diphenylmethane to benzene is plotted against the molecular weight of PC.

The relative retention time was adopted for compensa-

1) T. C. Davis, J. C. Peterson, and W. E. Haines, *Anal. Chem.*, **38**, 241 (1966).
2) A. Lavoie and J. E. Guillet, *Macromol.*, **2**, 445 (1969).
3) O. Smidsrød and J. E. Guillet, *ibid.*, **2**, 272 (1969).
4) S. Tsuge, T. Okumoto, Y. Sugimura, and T. Takeuchi, *J. Chromatogr. Sci.*, **7**, 253 (1969).

tion of small changes in the experimental conditions such as flow rate of carrier gas and column temperature.

We see from Fig. 2 that the polarity of MM-PC column decreases nearly hyperbolically with the increase of molecular weight. This is mainly due to the end hydroxy groups of MM-PC. On the other hand, the retention data of SM-PC shows relatively small changes because of the terminal *t*-butyl groups, whose polarity is smaller than that of the hydroxy group.

These data suggest that rough estimation of the molecular weight of PC is possible by this method, provided that the synthetic method is known.

Retention Behavior near T_g. The chain mobility of polymer varies considerably before and after T_g, which is expected to cause remarkable change of its interaction with the solute.

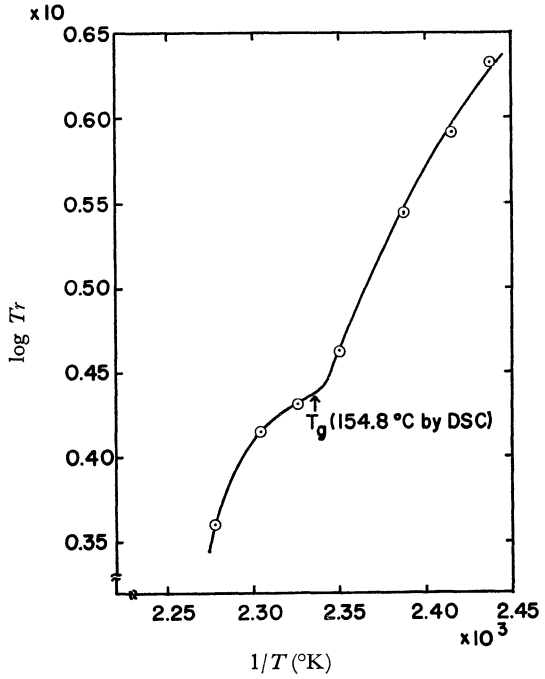


Fig. 3. The relationship between the reciprocal of the absolute column temperature and logarithms of the relative retention time (*Tr*) of *N,N*-dimethylformamide to cyclohexane near *Tg* for MM-PC.

Figure 3 shows the relationship between the reciprocal of the absolute column temperature and logarithms of the relative retention time of *N,N*-dimethylformamide to cyclohexane near T_g (154.8°C by DSC) for MM-PC. The relative retention time decreases with the rise of column temperature. However, a point of inflection exists near T_g. The same inclination was obtained for SM-PC. However, no appreciable differences were observed with variation of the molecular of PC.

Experimental

Materials. Fractionated PC-samples having molecular weights 10000—50000 were used. Raw PC was fractionated as reported previously[4] by successive precipitation method in methylene chloride-*n*-pentane system and the molecular weight of each fraction was measured by the viscosimetric method.

Preparation of Column Packing. PC weighting aboug 0.25 g was dissolved in 50 m*l* of methylene chloride. Then 0.75g of Celite 545 (80-100 mesh) was added to the solution. After the solvent was evaporated at 50°C in a vaccum with constant stirring, the coated support was packed in a column tube.

Gas Chromatographic Conditions. a) *For Measurement of Molecular Weight Effect*;
Gas chromatograph: Yanagimoto GCG Model 220 with TCD
Column: 2 mm, i. d. ×50 cm copper tube
Column temperature: 150 and 220°C
Carrier gas: H_2, 12 m*l*/min
Sample: mixture of benzene and diphenylmethane
Sample size: 10 μl

b) Measurement of Retention Behavior near T_g;
Gas chromatograph: Yanagimoto GCG 550 F with FID
Column: 2mn, i. d. ×100cm copper tube
Column temperature: 137—166°C
Carrier gas: N_2, 10ml/min
Sample: mixture of cyclohexane and *N,N*-dimethylformamide
Sample size: 0.1μl

c) Determination of Tg;
DSC: Rigaku Denki Model DT-10 Differential Scanning Calorimeter
Sample size: 25mg
Heating rate: 10°C/min