Thermally Dissociative Degradation of Polymers Containing Dicyclopentadiene Ring in Main Chains

Masatoshi MIURA, Fumihiko AKUTSU, Shigeo HIROSE, Yoshiyuki IKENO,
and Kuniharu NAGAKUBO

Department of Synthetic Chemistry, Faculty of Engineering, Chiba University, Yayoi-cho, Chiba 280

(Received December 13, 1976)

Polymers containing dicyclopentadiene units in their main chain were prepared by the polycondensation of dicyclopentadienedicarbonyl dichloride with bis(p-hydroxyphenyl) ether or 2,2-bis(p-hydroxyphenyl)propane. Thermal analysis showed that the dicyclopentadiene units dissociate reversibly. The results of thermal degradation in a nitrobenzene solution indicate that a reversible degradation occurs at 10% concentration of the polymer, and an irreversible one at concentration below 1%. The activation energy of the dissociation of dicyclopentadiene units in the main chain of the polymer was estimated to be 30 kcal/mol.

It is well-known that a molecule of dicyclopentadiene reversibly dissociates into two molecules of cyclopentadiene on heating. Thus, a polymer containing dicyclopentadiene ring in the main chain is expected to dissociate reversibly into polymers of lower molecular weight. Stille and Plummer attempted to synthesize polymer having such a structure by the Diels-Alder type polyaddition of bis(cyclopentadienyl)alkanes,[1] but obtained only polymers of low molecular weight. Thus the behavior of the thermally dissociative degradation of these polymers has not been clarified.

We obtained polymers of high molecular weight containing the dicyclopentadiene ring in the main chain by the polycondensation of dicyclopentadienedicarbonyl dichloride (DCPC) with bis(p-hydroxyphenyl) ether (HPE) or 2,2-bis(p-hydroxyphenyl)propane (HPP), and investigated their thermal behavior. This paper deals with thermally dissociative degradation of these polymers in solid state and in a nitrobenzene solution.

Experimental

Materials.   HPP was recrystallized from toluene just before use, mp 160—161 °C. HPE was prepared[2] from bis(p-aminophenyl) ether as a starting material *via* the diazonium salt and then acetate; it was recrystallized from water, mp 167—168 °C; 15% yield (based on the starting material). DCPC was obtained by the chlorination of dicyclopectadienedicarboxylic acid with thionyl chloride,[3] and recrystallized from petroleum ether, mp 61.5—62.5 °C (lit, 62 °C[3]).

Model compound (diphenyl dicyclopentadienedicarboxy-late). A solution of 2.21 g (8.9 mmol) DCPC in 10 ml dichloromethane was added to a mixture of 9.19 g (23.2 mmol) phenol, 3.23 ml (27.1 mmol) pyridine and 20 ml dichloro-methane at 19—23 °C, followed by stirring at the same temperature. The reaction mixture was washed with a dilute aqueous solution of sodium carbonate and then with water. The oily layer was separated and dried with anhy-drous calcium chloride, the solvent being removed. The viscous liquid so obtained was dissolved in methanol, poured into water to give a solid product, which was recrystallized from heptane to yield colorless crystals, mp 90.5—91.5 °C (lit, 92—94 °C[4]); 57.4% yield. Found: C, 77.38%; H, 5.32%. Calcd for $C_{24}H_{20}O_4$: C, 77.42%; H, 5.41%. The IR spectra showed absorptions for ester group at 1200 and 1735 cm^{-1} and for double bonds of dicyclopentadiene ring at 1600 and 1635 cm^{-1}.

Polycondensation.   A typical procedure is as follows. A solution of 0.643 g (2.5 mmol) DCPC in 3.8 ml dichloro-methane was added dropwise to a solution of 0.505 g(2.5 mmol) HPE and 0.8 ml (5.5 mmol) triethylamine in 7.5 ml dichloromethane under stirring at −3 °C. Stirring was continued for 45 min at −3——2 °C. The reaction mixture was poured into acetone containing 20% water to precipitate polymer. The polymer obtained was reprecipitated in benzene–methanol system and dried *in vacuo* to yield 80.8% of a white powdery polymer. The inherent viscosity(0.5% concn, *m*-cresol, 30 °C) was 0.67 dl/g. Found: C, 74.30%; H, 4.77%. Calcd for $C_{24}H_{18}O_5$: C, 74.60%; H, 4.70%. The IR spectra showed absorptions for the ester group at 1190 and 1700 cm^{-1} and for double bonds of the dicyclo-pentadiene ring at 1600 and 1630 cm^{-1}.

The polycondensation of DCPC with HPP gave high molecular weight polymers under the same reaction condi-tions as those described above except that reaction time was 10 minutes. The inherent viscosity (0.5% concn, *m*-cresol, 30 °C) was 0.84 dl/g. Found: C, 77.71%; H, 6.23%. Calcd for $C_{27}H_{24}O_4$: C, 78.62%; H, 5.86%. IR spectra showed not only the IR absorptions decribed for the polymer of DCPC with HPE, but also absorption for methyl group at 2960 and 1375 cm^{-1}.

Degradation and Measurement.   DTA and TGA were carried out on a Rigaku Denki thermal analyzer (Cat. No 8085D1) at a heating rate of 20 °C/min under a nitrogen stream.

Thermal degradation of a polymer solution was carried out in a sealed viscometer[5] for a dilute solution containing less than 1% of the polymer. A nitrobenzene solution of the polymer was added to the viscometer, degassed by a freeze-thaw procedure and sealed. The viscometer was heated at a specified temperature for a certain time, then rapidly cooled, viscosity being measured at 30 °C.

In the case of a solution of 10% concentration, a degassed polymer solution in a sealed glass tube was heated at a specified temperature for the desired time, and then diluted with nitrobenzene to 0.5%. The viscosity of the solution so obtained was measured at 30 °C with an Ubbelohde viscometer.

Results and Discussion

Preparation of Polymer.   The polycondensation of DCPC with bisphenol was carried out in dichloro-methane by low temperature solution polycondensation. The results are given in Table 1. The high molecular weight polymer of DCPC with HPE could be obtained at the reaction conditions of No. 5 in Table 1. With

TABLE 1. LOW TEMPERATURE SOLUTION POLYCONDENSATION OF DCPC WITH BISPHENOL
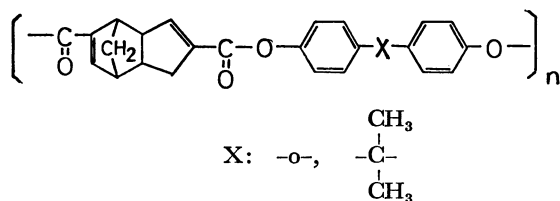
No.	Bispheonl	Concn of acid chloride[a] mol l^{-1}	Ratio of triethylamine to acid chloride mol mol^{-1}	Temp °C	Reaction time[b] h	Conversion %	η_{inh}[c] dl g^{-1}
1	HPE	0.167	2	2—3	1	76.4	0.12
2	HPE	0.187	2	1.5—3	6	60.1	0.11
3	HPE	0.220	2	2—3	1	78.1	0.40
4	HPE	0.220	2.2	−3——2	0.75	80.8	0.67
5	HPE	0.220	2.2	−3——2	2	—	—[d]
6	HPE	0.333	2	2—3	2	—	—[d]
7	HPP	0.220	2.2	−2——1	2	71.2	0.29
8	HPP	0.267	2.2	−3——1	0.16	61.1	0.84
9	HPP	0.267	2.2	−3——2	2	—	—[d]

a) Concn of acid chloride in reaction mixture. b) Reaction time after addition of acid chloride soln.
c) 0.5% *m*-cresol soln at 30 °C. d) Insoluble in *m*-cresol.

decrease in the concentrations of reactants, molecular weight of polymer decreased (Nos. 1 and 2). When the concentration of reactants was increased, a polymer insoluble in *m*-cresol was formed; it may be crosslinked (No. 6). An unnecessarily long reaction time also resulted in the formation of insoluble polymers. The polycondensation of DCPC with HPP proceeded in a similar way to that of DCPC with HPE with respect to the concentrations of reactants and the reaction time.

The resulting polymers were identified by elemental analysis and IR spectroscopy. Since the structure of DCPC was assigned by Peters[3,6] as endo-4,9-bis-(chloroformyl)tricyclo[5.2.1.0^{2,6}]deca-3,8-diene, the structures of the polymers obtained in this investigation are as follows.

$$\left[-\overset{\overset{H}{|}}{\underset{\underset{O}{\|}}{C}}\cdot\overset{}{\underset{}{(CH_2)}}\cdot\overset{}{\underset{\underset{O}{\|}}{C}}-O-\langle\rangle-X-\langle\rangle-O- \right]_n$$

X: -o-, $-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-$

Degradation in Solid State.   TGA and DTA curves of the model compound show two endothermic peaks at 92 and 190—305 °C respectively (Fig. 1, Curve A). The one at lower temperature corresponds to the melting point of the model compound. The other accompanied by 93% weight loss is due to the dissociation of the model compound and the volatilization of dissociated compounds. TGA and DTA of the polymer of DCPC with HPE show two endothermic peaks at 190—250 and 300—420 °C (Curve B). The first peak of curve B seems to be caused by the dissociation of polymer chains, since the thermal dissociation of the model compound starts at almost the same temperature. This was confirmed by the following experiment. Thus the polymer heated to 237 °C (at this temperature, the first endothermic peak can be observed, but not the second one) was allowed to cool down to room temperature; on reheating of this polymer, an endothermic peak appeared at 223—260 °C. The endothermic peak on reheating may be responsible for some chemical change of polymer by heating. The second peak at 300—420 °C accompanied by *ca.* 70% weight loss is
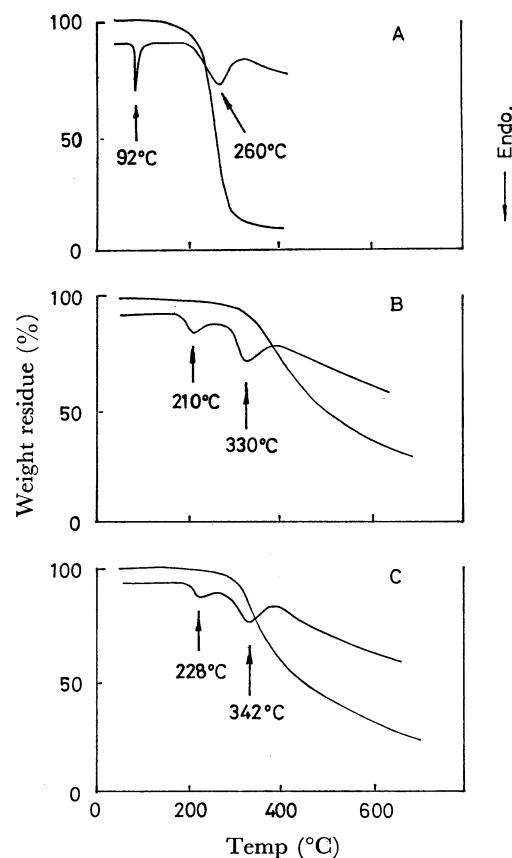

Fig. 1. TGA and DTA of model compound and polymers:
A, model compound;   B, polymer of DCPC with HPE
C, polymer of DCPC with HPP; N$_2$ flow, 100 ml/min;
rate of temperature increase, 20 °C/min.

due to further degradation and volatilization of dissociated and degradated fragments. TGA and DTA of the polymers of DCPC with HPP gave endothermic peaks at 190—250 and 250—400 °C accompanied by *ca.* 75% weight loss. The temperature at which the dissociation of polymer chains begins was similar to that for the polymers of DCPC with HPE, but endothermic peaks were observed at slightly higher temperature (Fig. 1).
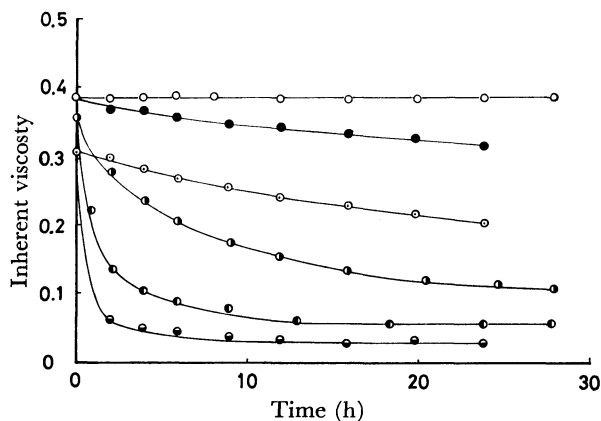
Degradation in a Solution.   Thermal degradation

Fig. 2. Effect of temperature on viscosity decrease of polymer: temperature; ○, 30 °C; ●, 40 °C; ◉, 50 °C; ◑, 60 °C; ◖, 80 °C; ◓, 100 °C; polymer concentration, 0.5%; samples of different molecular weight were used for the measurements at 50 and 60 °C.
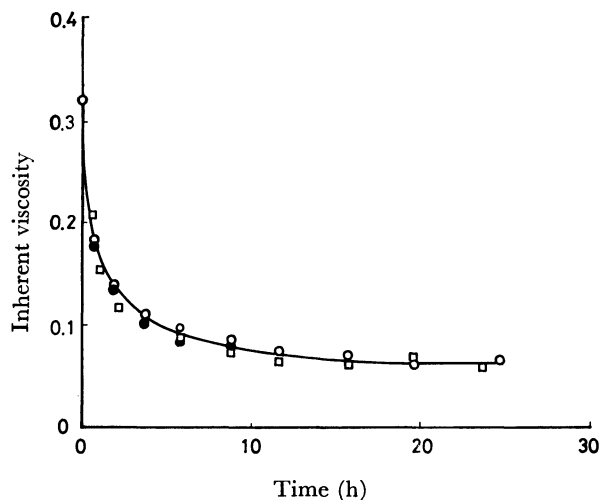

Fig. 3. Effect of polymer concentration on viscosity decrease of polymer at 80 °C: polymer concentration; ○, 1.0%; ●, 0.5%; □, 0.1%.
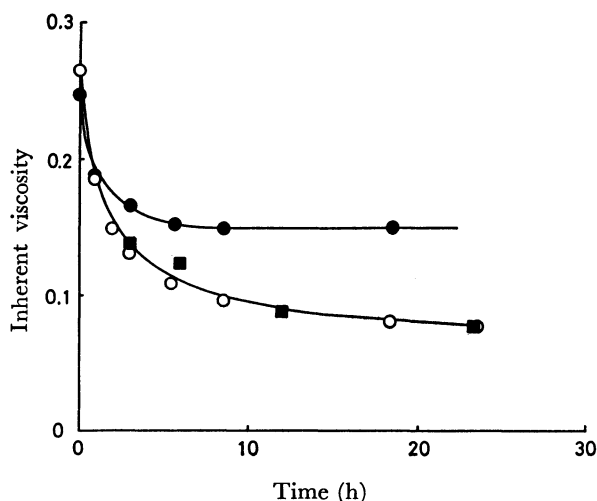

Fig. 4. Effects of polymer concentration and maleimide addition on viscosity decrease of polymer at 80 °C: ●, 10% polymer solution; ○, 1% polymer solution; ■, five times as much the molar quantity of N-phenylmaleimide as the dicyclophntadiene unit of the polymer was added to the 10% polymer solution. In the case of 10% polymer solutions viscosities were measured in 0.5%, and in the case of 1% no dilution was done.

processes of the polymers in a nitrobenzene solution were followed by viscometry. Figure 2 shows the viscosity change of a solution of the polymer of DCPC with HPE at a concentration of 0.5% at various temperatures. At 30 °C, no change in viscosity of the solution was observed for 30 h. This indicates that hardly any of the dicyclopentadiene ring in the main chains of the polymers dissociate at this temperature. With increasing temperature the viscosity decreased rapidly. At temperature higher than 80 °C, viscosity decreased a great deal at the initial stage of heating. When the polymers of DCPC with HPP were used, almost the same curves showing viscosity decrease as above were observed at 30 and 80 °C. Thus, further experiments were carried out on the polymers of DCPC with HPE only. For the polymer concentration from 0.1 to 1.0%, decrease in viscosity is not influenced by polymer concentration, (Fig. 3). This indicates that the polymer degrades irreversibly in a solution of concentration less than 1%. If the degradation of the polymer proceeds reversibly, the decay curve of the viscosity should be affected by the concentration of the polymer, since the forward reaction is of first-order with respect to the concentration of dicyclopentadiene unit and the reverse reaction is of second-order with respect to the concentration of cyclopentadienyl groups produced. Thermal degradation of the polymer in a solution of 10% concentration is shown in Fig. 4 together with that of the 1% polymer solution. In the case of the 10% polymer solution, the viscosity was measured for 0.5% polymer solution obtained by diluting the heat-treated 10% polymer solution with nitrobenzene. At 10% polymer concentration, viscosity fell to a constant value in a relatively short time, the value being higher than that of the 1% polymer solution. The 10% polymer solution heated for 18.5 h at 80 °C was allowed to stand for 48 h at room temperature, but no increase in viscosity of the polymer from the equilibrium value could be observed.

If the polymer is degraded in the presence of excess dienophile such as N-phenylmaleimide, cyclopentadienyl

groups produced by the dissociation of dicyclopentadiene units in the polymers react exclusively with N-phenylmaleimide; thus a recombination reaction of two cyclopentadienyl groups present as end groups of the degraded polymers would be disturbed. As shown in Fig. 4, addition of the maleimide to the 10% polymer solution has predominant effect of the decrease of molecular weight of the polymers. The decay curve of the viscosity in the presence of the maleimide was similar to that observed for the 1% polymer solution in which irreversibly dissociative degradation took place. The addition of maleimide to the 1% polymer solution had no effect on the relationship between the viscosity of the polymers and heating time.

From the effect of polymer concentration and that of maleimide addition on viscosity decrease, it is concluded that in the 10% polymer solution the degradation of the polymers proceeds by a reversible process, the molecular weight of the polymer reaching an equilibrium value. In this case, however, no viscosity recovery could be observed by letting the solution to stand for 48 h at room temperature. This might be responsible for the very slow rate of the recombination reaction because of the low reaction temperature. In a dilute solution below 1%, recombination of cyclopentadienyl groups is disturded by dilution; consequently irreversible degradation was observed.

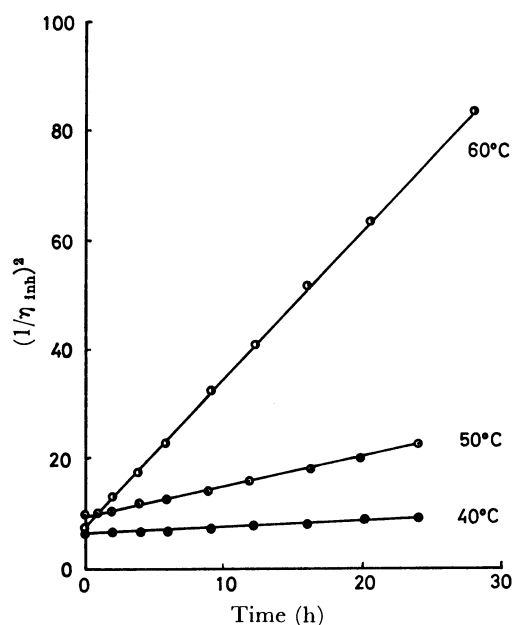If the polymers degrade irreversibly under random

Fig. 5. Plots of $(1/\eta_{inh})^2$ against time.

scission of the main chain, a linear relationship can be expected to exist between the reciprocal of the degree of polymerization and heating time. The plots of $(1/[\eta])^{1/\alpha}$ against heating time should be linear, where α donates the exponential term of the Mark-Houwink equation and $[\eta]$ intrinsic viscosity. However, α has not yet been estimated for this polymer solution. By assuming that α equals $1/2$, plots of $(1/\eta_{inh})^2$ against heating time were found to be linear at temperatures lower than 60 °C, using the data in Fig. 2, (Fig. 5). The Arrhenius plot of the slope of lines gave satisfactory linear relationship. The activation energy for the degradation of the polymer was calculated to be 30 kcal/mol. The activation energy corresponds to that for the dissociation of dicyclopentadiene units in the main chain of the polymer into cyclopentadienyl group, since the scission of the main chain seems to occur exclusively at the dicyclopentadiene units at a temperatures below 60 °C. The activation energy for the dissociation of dimethyl dicyclopentadienedicarboxylate was reported to be 30 kcal/mol in a tetraglyme solution.[7] It is interesting to note that the activation energy of the dissociation of dicyclopentadiene units in a polymer main chains agreed with that for a low molecular weight compound.

References

1) J. K. Stille, and L. Plummer, *J. Org. Chem.*, **26**, 4026 (1961).

2) G. Koga, M. Yasaka, and Y. Nakayama, *Org. prep. Proced.*, **1**, 205 (1969).

3) D. Peters, *J. Chem. Soc.*, **1960**, 1832.

4) W. E. Franklin, C. H. Mack, and S. P. Rowland, *J. Org. Chem.*, **33**, 626 (1968).

5) R. B. Mesrobian, and A. S. Tobolsky, *J. Polym. Sci.*, **2**, 463 (1947).

6) D. Peters, *J. Chem. Soc.*, **1960**, 1761.

7) W. E. Franklin and C. H. Mack, *Anal. Calorimetry Proc. Am. Chem. Soc. Symp.*, 155 th (1968) 181.