The Thermal Decomposition of Dicumyl Peroxide in Polyethylene Glycol and Polypropylene Glycol

P. D. ROWE and D. K. THOMAS, *Rubber and Plastics Research Association of Great Britain, Shawbury, Shrewsbury, Shropshire, England*

The effect of the free radicals produced by thermal decomposition of dicumyl peroxide, upon polyethylene glycol and polypropylene glycol has been studied. In the former the result was crosslinking and in the latter main-chain scission. The mechanisms of these reactions are discussed and a scission efficiency of unity is found in the latter case.

Dicumyl peroxide has application as a crosslinking agent in polyethylene[1,2] and ethylene–propylene copolymers.[3] Indications are that polypropylene undergoes degradation when heated with this peroxide.[3] Preliminary experiments carried out with polyethylene glycol (PEG) and polypropylene glycol (PPG) suggest that the former becomes crosslinked whilst the latter degrades. These materials can be obtained in low molecular weight liquid forms and are well suited to a study of the crosslinking and degradative reactions.

EXPERIMENT AND RESULTS

Samples of PEG and PPG containing up to 5 wt.-% of recrystallized dicumyl peroxide were placed in Pyrex tubes and thoroughly outgassed before sealing at 10^{-6} cm. Hg pressure. They were heated for known times in an oil bath at 140°C. and on withdrawal the decomposition of peroxide was suppressed by immersing the tubes in cold water. In those cases in which analysis of reaction products was required this was done immediately the sealed tubes were opened. In all cases the solubility of the product was examined and the limiting viscosity number of the solution measured.

Viscosity Measurements

Viscosities were measured in an Ubbelhode suspended-level viscometer at 25°C., water being used as a solvent for PEG and n-decane, or benzene for PPG. The limiting viscosity number was obtained by extrapolation of η_{sp}/c versus c where c is expressed in g./100 cc. For benzene solutions of PPG the number-average molecular weight was calculated from the relationship $[\eta] = 1.4 \times 10^{-4}M^{0.8}$ established by Ebert and Price.[4]

Analysis for Cumyl Alcohol and Acetophenone

In the case of PEG the products of reaction were identified as cumyl alcohol and acetophenone, and for quantitative work these were cold-

extracted from the polymer with isooctane (for UV analysis) and carbon tetrachloride (for IR analysis). The concentration of acetophenone was determined from the IR absorption at 1686 cm.$^{-1}$, and that of cumyl alcohol was subsequently obtained from the UV absorption at 2390 and 2640 A.

With PPG the soluble reaction products consisted of degraded polymer in addition to cumyl alcohol, acetophenone, and unchanged peroxide. The degraded polymer was readily soluble in all the common organic solvents; for a quantitative estimation of ketone and alcohol it was deemed necessary to separate them from the polymer. To simplify matters, quantitative analysis was made only with samples which had been heated to complete decomposition of the peroxide. Separation was performed by introducing the solution in isooctane onto a silicic acid column and eluting with isooctane; a good separation of cumyl alcohol and acetophenone from the polymer was obtained, and the amount of each was calculated from the UV absorption at 2390 and 2640 A.

The UV absorption measurements were made with a Unicam SP 500 spectrophotometer and IR absorptions with a Grubb-Parsons double-beam instrument and a rock salt prism. It was verified that at the wavelengths used in quantitative analysis all the components obeyed Beer's law separately and in admixture over the concentration ranges encountered in this work.
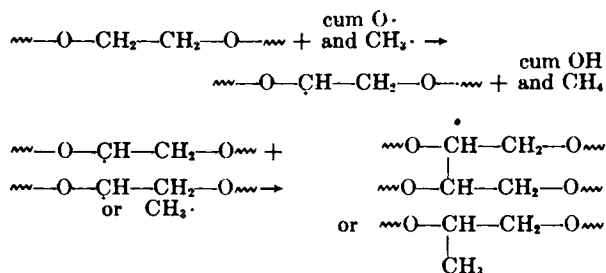
DISCUSSION

Polyethylene Glycol

The results given in Table I together with the fact of decreasing solubility of the polymer are consistent with the view that polyethylene glycol undergoes a crosslinking reaction when heated with dicumyl peroxide. A stage is reached at which some of the polymer becomes completely insoluble; for example, heating for $2^1/_2$ hr. at 140°C. with 3 wt.-% of peroxide produced a gel fraction of 20% which displayed limited swelling in water over several weeks. Quantitative analytical work on PEG of M.W. 4000, heated with 5 wt.-% of peroxide, gave a value of 0.38 for the ketone/alcohol ratio, and this is of the same order as the values 0.45 and 0.43 obtained for polyethylene[5] at 135°C. and n-decane[6] at 140°C. The value of this ratio gives a rough indication of the reactivity of the secondary hydrogen atoms to the cumyloxy radical, and it follows that in so far as abstraction by a free radical is concerned the secondary hydrogen atoms in ethers and alkanes are of comparable reactivity. Other evidence for this has been reported from studies of hydrogen abstraction by methyl radicals from low molecular weight ethers and alkanes.[7,8] It is probable that these reactions involving a free radical are sufficiently facile to obscure those differences in reactivity which undoubtedly exist between the hydrogen atoms in ethers and alkanes. The fact that virtually all the decomposed peroxide is recovered as acetophenone or cumyl alcohol (see Table II)

TABLE I
Limiting Viscosity Numbers of PEG and PPG after Heating
with Dicumyl Peroxide at 140°C.

M.W.	Peroxide, Wt.-%	Fraction of peroxide decompd.	Solvent	$[\eta]$ at 25°C.
		Polyethylene Glycol		
400	5	0	Water	0.036_2
400	5	0.95_5	"	0.042_5
4000	1.5	0	"	0.124
4000	1.5	0.81_5	"	0.135
4000	3	0.88	"	0.151 (sol fraction)
		Polypropylene Glycol		
2500	3	0	n-Decane	0.044
2500	3	0.98	"	0.035_4
2500	5	0.41	"	0.041
2500	5	0	Benzene	0.075
2500	5	0.61_7	"	0.062
2500	5	0.86_6	"	0.056_5

is a good indication that no cumyloxy groups become attached to the cross-linked polymer. A reaction mechanism consistent with these results is:

$$\text{ww—O—CH}_2\text{—CH}_2\text{—O—ww} + \begin{array}{c}\text{cum O·} \\ \text{and CH}_3\text{·}\end{array} \rightarrow$$

$$\text{ww—O—CH—CH}_2\text{—O—ww} + \begin{array}{c}\text{cum OH} \\ \text{and CH}_4\end{array}$$

$$\begin{array}{l}\text{ww—O—CH—CH}_2\text{—O—ww} + \\ \text{ww—O—CH—CH}_2\text{—O—ww} \rightarrow \\ \qquad\text{or} \quad \text{CH}_3\text{·}\end{array}$$

$$\begin{array}{l}\text{ww—O—CH—CH}_2\text{—O—ww} \\ \qquad | \\ \text{ww—O—CH—CH}_2\text{—O—ww} \\ \text{or} \quad \text{ww—O—CH—CH}_2\text{—O—ww} \\ \qquad\qquad\qquad\quad | \\ \qquad\qquad\qquad\quad\text{CH}_3\end{array}$$

The termination reactions lead to the formation of crosslinked polymer and polypropylene glycol; the latter reaction is unlikely to occur to any significant extent because of the much greater concentration of secondary hydrogen atoms available for reaction with the methyl radical.

All those cumyloxy radicals failing to abstract hydrogen decompose to give methyl radicals which may abstract hydrogen or dimerize to ethane. Using molecular scale models and assuming a linear zigzag structure for the polymer we found that the approach of a cumyloxy radical to the methylene hydrogens is slightly hindered. The presence of a fairly high concentration of acetophenone amongst the reaction products is therefore not surprising.

Polypropylene Glycol

The effect upon $[\eta]$ of heating with dicumyl peroxide is shown in Table I; the solubility of the polymer in such solvents as benzene, isooctane,

TABLE II

Ratio of Acetophenone to Cumyl Alcohol in Polyethylene Glycol at 140°C.

M.W.	Peroxide, wt.-%	Fraction of peroxide decompd.	Ketone in extract concn., g. mole/l.	Alcohol in extract concn., g. mole/l.	Ketone/alcohol	Peroxide accounted for, %
4000	5	0.49	0.493×10^{-2}	1.332×10^{-2}	0.37	100
"	"	0.60_6	0.612×10^{-2}	1.571×10^{-2}	0.39	99
"	"	0.97_8	0.970×10^{-2}	2.504×10^{-2}	0.38_7	96

TABLE III

Ratio of Acetophenone to Cumyl Alcohol in Polypropylene Glycol at 140°C.

M.W.	Peroxide, wt.-%	Fraction of peroxide decompd.	Ketone in eluent, g. mole/l.	Alcohol in eluent, g. mole/l.	Ketone/alcohol	Peroxide accounted for, %
2500	5	~1.0	2.50×10^{-4}	1.80×10^{-4}	1.39	102
"	5	~1.0	2.68×10^{-4}	2.06×10^{-4}	1.30	95

propanol, acetone, and water also increases.   This suggests that main-chain scission is occurring.   The IR absorption spectrum of PPG during the reaction displays one interesting feature: reference to Figure 1 shows the
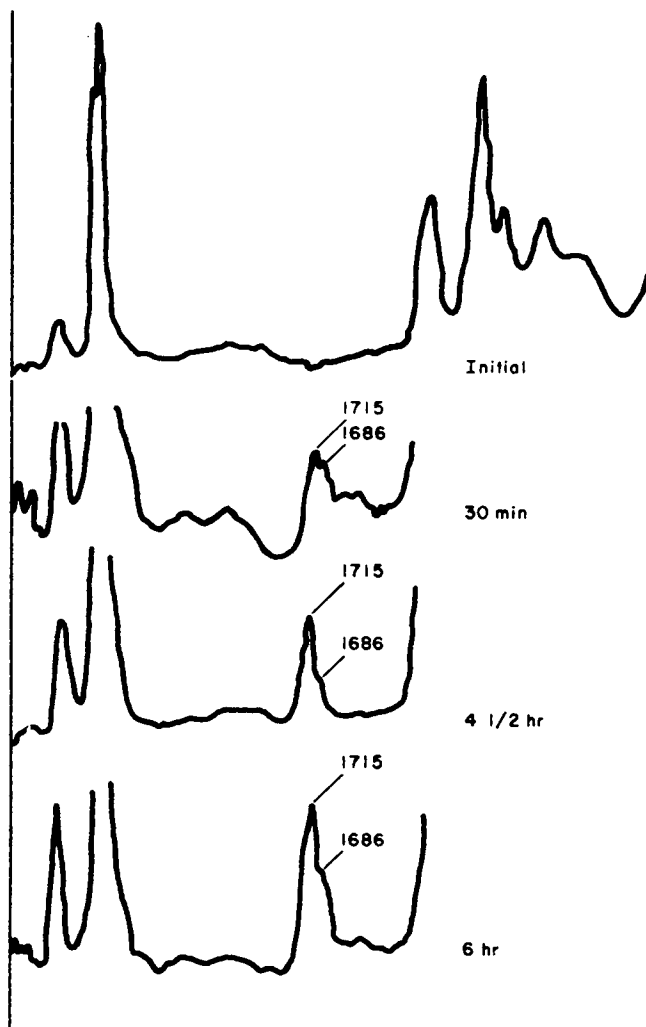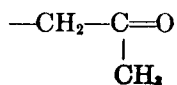

Fig. 1. Infrared spectrum of PPG at intervals during degradation.

gradual development of a band at 1715 cm.$^{-1}$, which is close to but distinguishable from the band at 1686 cm.$^{-1}$ due to C=O in acetophenone. Absorption at 1715 cm.$^{-1}$ may be due to an aliphatic carbonyl such as

$$-CH_2-C=O$$
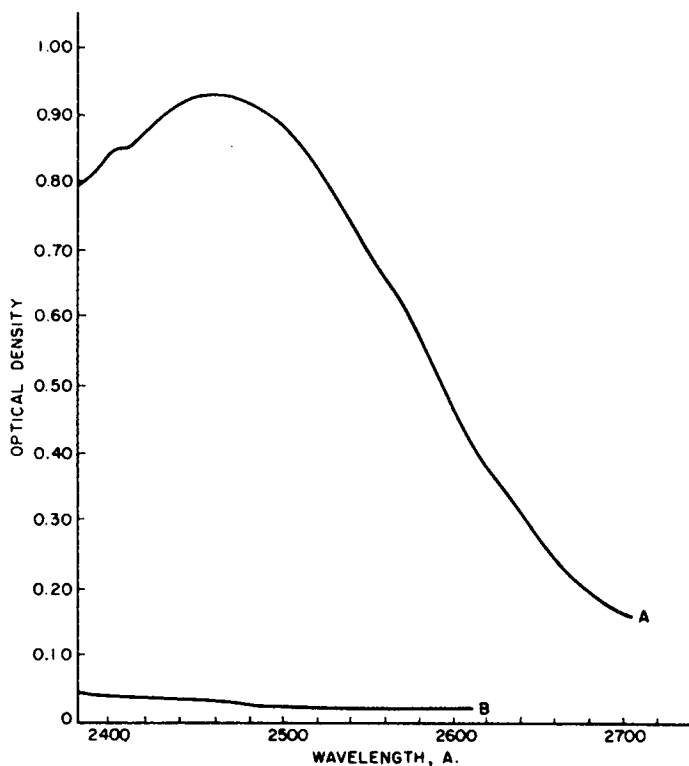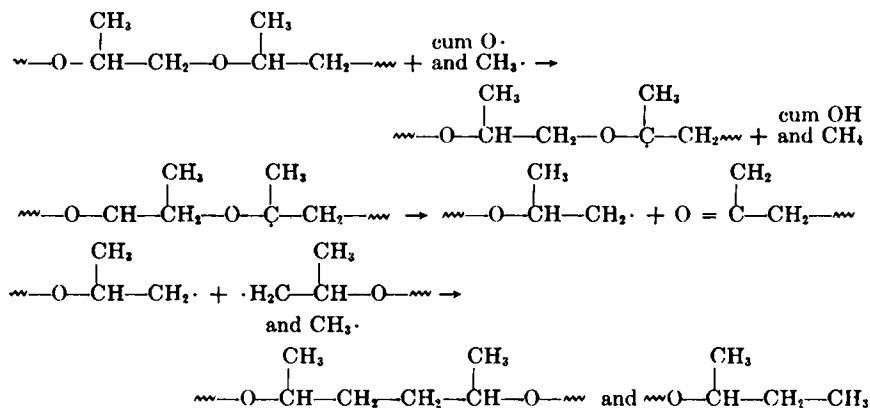$$|$$
$$CH_3$$

Fig. 2. Ultraviolet absorption spectrum of PPG: (A) water eluent from silicic acid column; (B) initial, in MeOH.

In two cases the cumyl alcohol and acetophenone were separated from the degraded polymer; the results of the spectroscopic analysis are shown in Table III. The value obtained for the ketone/alcohol ratio is 1.39 at 140°C. and the recovery of peroxide is virtually complete (100 ± 5%). Hence no cumyloxy radicals become attached to the polymer during reaction, a conclusion supported by the UV absorption spectrum of the degraded polymer, shown in Figure 2. Although the absorption is higher than for the original material (probably owing to carbonyl groups in the degraded material and, possibly, to some unextracted acetophenone), there is no sign of fine structure in the 2500–2650 A. region such as is shown by the cumyloxy grouping.

It should be noted that despite the presence of a tertiary hydrogen atom on every fourth atom in the main chain the ketone/alcohol ratio is much higher than in the case of polyethylene glycol. Construction of a molecular model shows that the cumyloxy radical can make a reasonably free approach to the tertiary hydrogen but is hindered considerably in approaching the two secondary hydrogens. It follows that PEG contains a much greater proportion of reactive hydrogen than does PPG, and this would lead to a lower ketone/alcohol ratio in the former.

The following reaction mechanism is consistent with the experimental findings:

$$\begin{array}{ccc} \text{CH}_2 & \text{CH}_3 \\ | & | \\ \text{\textasciitilde---O--CH--CH}_2\text{--O---CH--CH}_2\text{---\textasciitilde} & + & \text{cum O} \cdot \\ & & \text{and CH}_3 \cdot \rightarrow \end{array}$$

$$\begin{array}{cc} \text{CH}_3 & \text{CH}_3 \\ | & | \\ \text{\textasciitilde---O--CH--CH}_2\text{--O--C--CH}_2\text{\textasciitilde} & + \begin{array}{c}\text{cum OH}\\\text{and CH}_4\end{array} \end{array}$$

$$\begin{array}{cc} \text{CH}_3 \quad \text{CH}_3 & \text{CH}_3 \qquad \text{CH}_2 \\ | \quad\quad | & | \qquad\quad || \\ \text{\textasciitilde---O--CH--CH}_2\text{--O--C--CH}_2\text{---\textasciitilde} \rightarrow \text{\textasciitilde---O--CH--CH}_2 \cdot + \text{O} = \text{C--CH}_2\text{---\textasciitilde} \end{array}$$

$$\begin{array}{cc} \text{CH}_2 & \text{CH}_3 \\ | & | \\ \text{\textasciitilde---O--CH--CH}_2\cdot + \cdot\text{H}_2\text{C--CH--O---\textasciitilde} \rightarrow \\ \text{and CH}_3\cdot \end{array}$$

$$\begin{array}{ccc} \text{CH}_3 & \text{CH}_2 & \text{CH}_3 \\ | & | & | \\ \text{\textasciitilde---O--CH--CH}_2\text{--CH}_2\text{--CH--O---\textasciitilde} & \text{and \textasciitilde-O--CH--CH}_2\text{--CH}_3 \end{array}$$

From a knowledge of the rate of decomposition of dicumyl peroxide[9] and the change in number average molecular weight of the polymer the scission efficiency can be calculated. The results are given in Table IV and they show that to within the limits of experimental accuracy one main chain break occurs for each molecule of peroxide decomposed, i.e., a scission efficiency of unity.

The presence of an oxygen atom in the main chain, which permits the polymer radical to rearrange to a ketone and a primary radical, undoubtedly contributes towards the high efficiency of the scission process.

The relevance of these results to the case of polyethylene and polypropylene arises from the fact that the structural difference between them is exactly the same as for PEG and PPG. This difference, in the case of PEG and PPG, leads to important changes in the reactions of the polymer radicals formed on hydrogen abstraction. The failure of PPG to crosslink must be due to an inability of the polymer radicals to orientate themselves suitably owing to free rotation of the methyl groups about the carbon atom carrying the free radical. This condition will definitely arise in polypropylene but, owing to the absence of oxygen in the main chain, it is unlikely that the scission efficiency will be as high as in PPG for an equivalent concentration of radicals.

TABLE IV

Scission Efficiency of Dicumyl Peroxide in Polypropylene Glycol

Init. M.W.	Fraction of peroxide decompd.	Final M.W.	Scission efficiency, %
2.576×10^3	0.44	2.193×10^3	86
2.576×10^3	0.61_5	2.032×10^3	91
2.576×10^3	0.86_5	1.807×10^3	103
			Mean, 90

References

1. Dannenberg, E. M., M. E. Jordan, and H. M. Cole, *J. Polymer Sci.*, **31**, 127 (1958).

2. Amberg, L. O., and W. D. Willis, *Proc. Intern. Rubber Conf.*, Washington, D. C., Nov. 1959.

3. Natta, G., G. Crespi, and M. Truzzonl, *Kautschuk u. Gummi*, **14**, WT54 (1961).

4. Ebert, P. E., and C. C. Price, *J. Polymer Sci.*, **34**, 157 (1959).

5. Dannenberg, E. M., M. E. Jordan, and H. M. Cole, *J. Polymer Sci.*, **31**, 127 (1958).

6. Thomas, D. K., unpublished results.

7. Trotman-Dickenson, A. F., and E. W. R. Stercie, *J. Chem. Phys.*, **19**, 329 (1951).

8. Trotman-Dickenson, A. F., *Quart. Rev.*, **7**, No. 2, 198 (1953).

9. Thomas, D. K., unpublished results.

Synopsis

The changes in solvent resistance and solution viscosity of polyethylene glycol and polypropylene glycol after heating with dicumyl peroxide at 140°C. are consistent with crosslinking of the former and degradation of the latter. Analytical work showed that in both cases all of the peroxide decomposed could be accounted for acetophenone and cumyl alcohol. In the case of polyethylene glycol, crosslinking results from abstraction of secondary hydrogen atoms and dimerization of the resulting radicals; in the case of polypropylene glycol abstraction of tertiary hydrogen atoms leads to radicals which break down by scission at a C—O bond to give a ketone and a more stable radical. This latter process proceeds with an efficiency of unity.

Résumé

Les changements observés dans la résistance aux solvants et dans la viscosité de la solution du polyéthylène glycol et du polypropylène glycol après chauffage à 140°C en présence de peroxyde de dicumyle sont en accord avec l'hypothése d'un pontage dans le premier cas et d'une dégradation dans l'autre. Dex trauvx analytiques ont montré que dans les deux cas les produits de décomposition du peroxyde sont l'acétophénone et le phényldiméthyl-carbinol. Dans le cas du polyéthylène glycol, le pontage résulte de l'arrachement des atomes d'hydrogène secondaires et de la dimérisation des radicaux qui en résultant tandes que dans le cas des polypropylènes l'arrachement des atomes d'hydrogène tertiaires produit des radicaux qui disparaissent par scission de la liaison C—O pour donner une cétone et un radical plus stable. Ce dernier processus a lieu avec une efficacité égale à l'unité.

Zusammenfassung

Die Änerung der Lösungsmittelbeständigkeit und Lösungsviskosität von Polyäthylenglykol und Polypropylenglykol nach Erhitzen mit Dicumylperoxyd bei 140°C ist konsistent mit einer Vernetzung des ersteren und einem Abbau des letzteren. Die Analyse zeigte, dass in beiden Fällen das gesamte zersetzte Peroxyd als Acetophenon und Cumylalkohol wiedergefunden wird. Im Fall des Polyäthylenglykols kommt die Vernetzung durch die Abspaltung von sekundären Wasserstoffatomen und Dimerisation der resultierenden Radikale zustande, während bei Polypropylenglykol die Abspaltung von tertiären Wasserstoffatomen zu Radikalen führt, die durch Spaltung an der C—O, Bindung unter Bildung eines Ketons und eines stabileren Radikals zerfallen. Dieser Prozess verläuft mit einer Ausbeute von eins.