REACTIONS OF CUMYLOXYL RADICALS WITH TETRAKIS(ALLYLOXYMETHYL)METHANE

Ivan CHODÁK, Dušan BAKOŠ and Edita ZIMÁNYOVÁ
Polymer Institute, Slovak Academy of Sciences, 809 34 Bratislava

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GLC Analysis of decomposition products of dicumyl peroxide has been used for determination of relative rate constant of hydrogen transfer of cumyloxyl radicals with tetrakis(allyloxymethyl)-methane. This constant is 15 times higher than that with 2,2,4-trimethylpentane. In the reaction an only small portion of the oxyl radicals (up to 15% of total amount) is consumed by addition to allyl groups of the monomer even when a great excess of the latter is present in the reaction mixture.

Polyfunctional monomers are used as additives for modification of polymers produced by radical-initiated polymerizations. Their main purpose is formation of three-dimensional structure, *i.e.* insoluble portions.

Efficiency of the cross linking of polymers initiated by thermal decomposition of peroxides is considerably increased by addition of a polyfunctional monomer[1,2].

Often gel is produced in a polymer which does not undergo cross linking without additives or is even degradated[3]. The proper mechanism of reaction of the monomer in the modification initiated by free radicals can be complex, various side reactions being possible, especially the transfer reaction of the primary radical with the monomer and homopolymerization of the monomers.

This paper deals with reaction of cumyloxyl radicals with a four-functional monomer — tetrakis(allyloxymethyl)methane.

EXPERIMENTAL

Dicumyl peroxide was purified by recrystallization from ethanol, tetrakis(allyloxymethyl)methane was synthetized from allyl bromide and pentaerythritol according to ref.[4]. Amounts of the reaction products — cumyl alcohol (CA) and acetophenone (AP) were determined by gas chromatography at 140°C in a 150 cm column packed with WAW Chromosorb containing 15% neopentyl glycol sebacate. The thermal decomposition of dicumyl peroxide in the respective solvents was carried out in glass ampoules under nitrogen at 145°C for 5 h.

The relative rate constants of the transfer reaction of the oxyl radicals with medium were calculated from the determined amount of the formed reaction products (CA, AP) from the reactions:

$$Ph(CH_3)_2CO\cdot + SH \xrightarrow{k_t} Ph(CH_3)_2COH + S\cdot$$

$$Ph(CH_3)_2CO\bullet \xrightarrow{k_f} Ph(CH_3)C{=}O + \bullet CH_3\,,$$

where SH means the reaction medium containing reactive hydrogen atom. The alcohol to ketone ratio gives immediately the relative reactivity of medium[5]:

$$[CA]/[AP] = k_t[SH]/K_f\,. \qquad (1)$$

If the medium is a mixture of several compounds, then the term $k_t[SH]$ represents an additive quantity[5]:

$$k_t[SH] = k'_t[S_1H] + k''_t[S_2H] + \ldots\,, \qquad (2)$$

where k'_t, k''_t are the transfer rate constants to the hydrocarbons S_1H, S_2H *etc.*, respectively.

RESULTS AND DISCUSSION

From Table I it is seen that in pure 2,2,4-trimethylpentane the ratio $[CA]/[AP]$ equals 0·207, being independent of the peroxide concentration. In the presence of 1% of tetrakis(allyloxymethyl)methane (TM) the value $[CA]/[AP]$ increased to 0·267, and within 0·02 to 0·15 mol l^{-1} of peroxide concentration it is independent of the initiator, too. With respect to Eq. (*2*) the difference 0·06 between the value in pure 2,2,4-trimethylpentane and that in the presence of tetrakis(allyloxymethyl)methane represents the term $k'_t[TM]/k_f$. As k_f is independent of the solvent composition[6], it can be calculated $k'_t = 15k_t$.

TABLE I

Ratio of the Formed Cumyl Alcohol (CA) and Acetophenone (AP) from Dicumyl Peroxide (DP) at 145°C in Pure 2,2,4-Trimethylpentane (A) and in the Presence of 1% Tetrakis(allyloxymethyl)-methane (B)

[DP] mol l^{-1}	[CA]/[AP], mol l^{-1}	
	A	B
0·02	—	0·271
0·04	—	0·258
0·05	0·205	—
0·06	—	0·260
0·08	—	0·265
0·10	0·206	0·274
0·125	—	0·274
0·15	0·210	0·267
average	0·207	0·267

A similar k_t' value was also obtained from the dependence of $[CA]/[AP]$ on solvent composition (Fig. 1). The solvent was a mixture of 2,2,4-trimethylpentane and benzene in which $0{\cdot}1 \text{ mol l}^{-1}$ dicumyl peroxide was decomposed in the presence of 1% tetrakis(allyloxymethyl)methane. The intercept at the ordinate is equal to 0·068 in this case, and it again corresponds to the sum $(k_t'[TM] + k_t[SH])^+/k_f$. The term

TABLE II

Sum of Cumyl Alcohol (CA) and Acetophenone (AP) after Decomposition of 0·1M Dicumyl Peroxide in 2,2,4-Trimethylpentane in the Presence of Tetrakis(allyloxymethyl)methane (TM)

[TM] %	[CA] + [AP] mol l^{-1}	[TM] %	[CA] + [AP] mol l^{-1}
0	0·205	1·0	0·184
0·10	0·204	2·5	0·186
0·25	0·207	5·0	0·170
0·50	0·206	10·0	0·177
0·75	0·209		

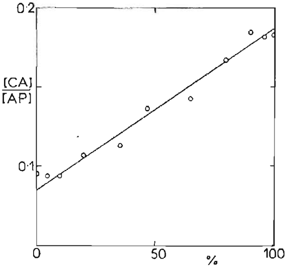

FIG. 1

Dependence of [CA]/[AP] Ratio on Composition of Solvent (2,2,4-Trimethylpentane–Benzene) in the Presence of 1% Tetrakis-(allyloxymethyl)methane

$[DP]_0 = 0{\cdot}1 \text{ mol l}^{-1}$, 145°C, 5 h.

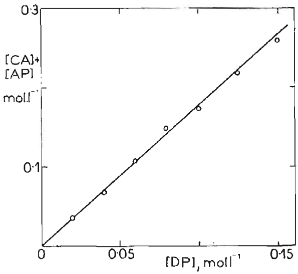

FIG. 2

Dependence of Sum ([CA] + [AP]) on Initial Concentration of Dicumyl Peroxide at $[TM]_0 = 1\%$, 145°C, 5 h

k_t[SH] corresponds to pure benzene and can be practically neglected, being of 10^{-3} to 10^{-4} order of magnitude[7]. Thus the extrapolated value 0·068 agrees satisfactorily with the value 0·06 calculated from the abovementioned data.

Comparison of amount of the reaction products with the initial concentration of cumyl peroxide can give information about the addition reaction of cumyloxyl radicals with tetrakis(allyloxymethyl)methane. In the medium of a saturated hydrocarbon the sum of molar concentrations [CA] + [AP] equals theoretical value of double initial concentration of dicumyl peroxide[8], so that the determined decrease for the reaction carried out in the presence of tetrakis(allyloxymethyl)methane can be immediately ascribed to primary addition of RO• radicals to double bonds of the monomer. Dependence of this sum on the initial dicumyl peroxide concentration is given in Fig. 2, the tetrakis(allyloxymethyl)methane concentration being 1%. Out of total amount of the cumyloxyl radicals formed, about 10% are consumed by addition. Furthermore, from Table II we can see the influence of the monomer concentration on the sum [CA] + [AP]. Increasing monomer concentration results in acceleration of the addition, but the amount of the radicals added does not exceed 15% of total amount even in the presence of 10% tetrakis(allyloxymethyl)methane in solution. From Fig. 3 it is seen that change in the initial concentration of tetrakis-(allyloxymethyl)methane causes a change in the [CA]/[AP] ratio. At low concentrations of the monomer the dependence is roughly linear with a slope 0·072. Physical

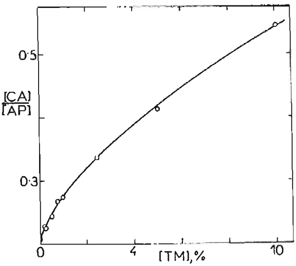

FIG. 3

Dependence of [CA]/[AP] Ratio on Amount of the Present Tetrakis(allyloxymethyl)-methane in 2,2,4-Trimethylpentane
[DP]$_0$ = 0·1 mol l^{-1}, 145°C, 5 h.

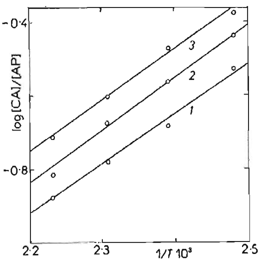

FIG. 4

Dependence of log ([CA]/[AP]) on Temperature in Pure 2,2,4-Trimethylpentane (*1*), with 1% Tetrakis(allyloxymethyl)methane (*2*), and with 2·5% TM (*3*).

meaning of this slope is given by the expression $k'_{t}[\mathrm{TM}]/k_{f}$, and its value approaches the values 0·06 and 0·068 obtained from the abovementioned data.

At higher concentrations of tetrakis(allyloxymethyl)methane a marked deviation from linearity was observed; a polymer insoluble in usual solvents (probably with three-dimensional structure) being precipitated from the solution. The amount of the polymer approached to that of initial monomer in the solution. From these facts it can be deduced that the decrease of reactivity of the medium (Fig. 3) is due to precipitation of the major part of the monomer from the solution.

However, the polymerization is not predominantly initiated by the primary radicals, because it was shown that their addition to the monomer takes place to a small extent only. Besides the kinetic chain is short with allyl monomers[9]. Obviously the formation of polymer is assisted significantly by addition of the secondary alkyl radicals, *i.e.* methyl radicals from fragmentation of the primary oxyl radicals or radicals from medium formed by the transfer reaction of RO· with the present 2,2,4-trimethylpentane. A certain portion of the polymer formed is undoubtedly due to recombination of the radicals produced by fast transfer reaction of the monomer with the primary oxyl radicals.

Finally we also investigated influence of temperature on the [CA]/[AP] ratio: Fig. 4 represents the temperature dependence of log ([CA]/[AP]) for various concentrations of the monomer. From these results it follows that the difference of the activation energies of the fragmentation and the transfer is $E_f - E_t = 28 \text{ kJ mol}^{-1}$. This value agrees with that found for saturated hydrocarbons, *e.g.* cyclohexane[5]. From Fig. 4 it can be seen that addition of tetrakis(allyloxymethyl)methane of the concentration used causes no significant deviations of the $(E_f - E_t)$ value from that found in pure hydrocarbon.

From the results it follows that the reaction of the oxyl radicals with the allyl hydrogen atoms of tetrakis(allyloxymethyl)methane is by one order of magnitude faster than that with saturated hydrocarbons. This data disagree with those by Rado[1] who did not find any acceleration of the transfer reaction in the presence of 2,4,6-triallyloxy-1,3,5-triazine (triallyl cyanurate). Hence it follows that application of polyfunctional monomers of similar type can result in entirely different course of the transfer reactions, whereby sometimes the whole process can be considerably affected.

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