

# Free radical polymerization of unconjugated dienes: 19. Temperature dependence of the cyclopolymerization of *o*-divinylbenzene

Luigi Costa, Oscar Chiantore and Marino Guaita

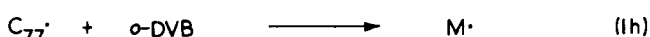
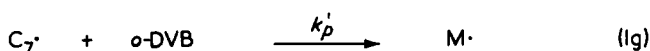
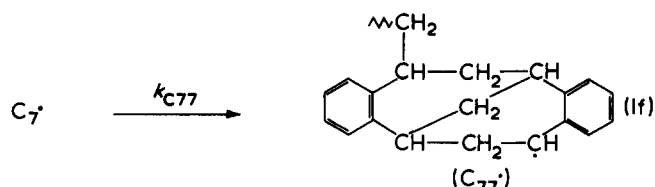
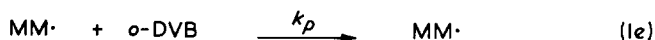
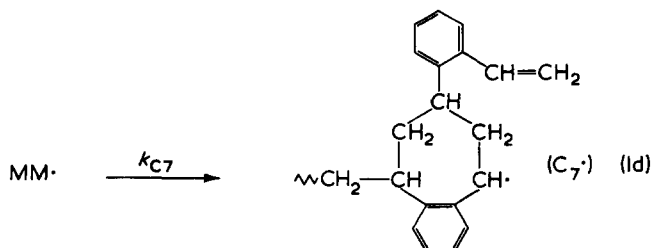
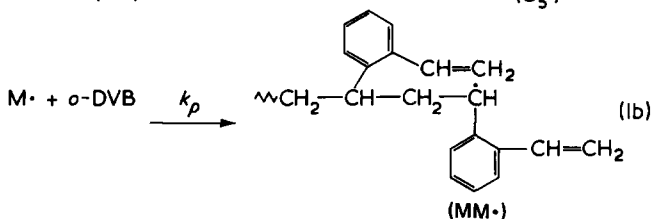
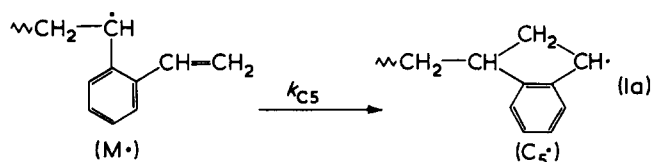
Istituto di Chimica Macromolecolare dell'Università di Torino, Via G. Bidone, 36, 10125 Torino, Italy

(Received 3 August 1977; revised 27 September 1977)

The temperature dependence of the extent of cyclization in the free radical polymerization of *o*-divinylbenzene has been investigated. The results have been interpreted on the basis of a kinetic relationship derived by assuming that three different cyclization reactions can occur during the chain growth: it has been found that of these reactions one largely prevails over the others. The difference between the activation energy of the main cyclization reaction and that of the intermolecular addition of the growing chain onto a monomer molecule compares well with the analogous differences already found in the cyclopolymerizations of acrylic and methacrylic anhydrides. The corresponding difference between the activation entropies is in highly satisfactory agreement with the one which can be calculated for the formation of a seven-membered ring structure. Both these facts strongly support the hypothesis that, in the main cyclization reaction occurring in the free radical polymerization of *o*-divinylbenzene, benzocycloheptene structures, practically free of strain, are formed.

## INTRODUCTION

It has been shown in a previous paper<sup>1</sup> that the residual unsaturation content in the products of the free radical polymerization at 70°C of *o*-divinylbenzene (*o*-DVB) can be adequately interpreted on the basis of the following chain propagation reactions:



Such a propagation mechanism can be considered as the superposition of the cyclopolymerization which is typical of 1,5- and 1,6-dienes, in which the intramolecular cyclization reactions involving only one monomeric unit are of the type of reaction (1a), and the cyclopolymerization of 1,4-dienes characterized by cyclization reactions similar to reactions (1d) and (1f), which involve the two monomeric units last entered in the polymer chain. The experimental data obtained from the study of the free radical polymerization at 70°C of *o*-DVB show that reaction (1d) should be the main cyclization process, reactions (1a) and/or (1f) becoming relevant only at very low monomer concentration.

The temperature dependence of the free radical polymerization of *o*-DVB has been now investigated, with the aim of checking if the tendency of this monomer to yield cyclic structural units might be interpreted, as in the case of other cyclopolymerization processes<sup>2,3</sup>, on the basis of the difference between the activation entropies of the intramolecular cyclizations and the intermolecular additions of the growing polymer chain on a monomer molecule. The results obtained are reported and discussed in the present paper.

Table 1 Mole fraction  $f_U$  of residual unsaturations in the polymers obtained at different temperatures from *o*-DVB in toluene solutions of molar concentration [M]

Temperature of polymerization (°C)							
70		60		50		35	
[M]	$[f_U]$	[M]	$[f_U]$	[M]	$[f_U]$	[M]	$[f_U]$
0.064	0.293	0.185	0.435	0.131	0.347	0.334	0.481
0.116	0.405	0.272	0.466	0.176	0.383	0.684	0.518
0.181	0.442	0.425	0.488	0.279	0.441	0.993	0.558
0.319	0.456	0.682	0.532	0.425	0.447	1.337	0.585
0.713	0.492	1.300	0.570	0.655	0.509	2.021	0.641
1.290	0.542			1.315	0.563		
1.621	0.569			1.63*	0.575*		
1.994	0.591			1.999	0.617		
2.62*	0.602*			2.48*	0.635*		
4.09*	0.713*						

\* Data reported in ref 4

## EXPERIMENTAL

The free radical polymerizations of *o*-DVB in toluene solutions were carried out following the procedure already described<sup>1</sup> at 70°, 60°, 50° and 35°C. The monomer concentration in the polymerization mixture was evaluated at the reaction temperature, taking into account the expansion of the solutions of *o*-DVB in toluene. The residual unsaturation content in the polymerization products was determined by bromination, as previously reported<sup>1</sup>.

## RESULTS AND DISCUSSION

The results of the determination of the residual unsaturation content in the products of the free radical polymerization at different temperatures of *o*-DVB in toluene solutions are collected in Table 1. The residual unsaturation content is expressed as the mole fraction  $f_U$  of monomeric units formed by *o*-DVB molecules which have contributed to the polymer chain growth with only one of their unsaturations. In Table 1 are also reported the data by Aso, Nawata and Kamao<sup>4</sup>, relative to the products of the free radical polymerization, at low monomer to polymer conversion, of *o*-DVB in benzene solutions.

It has been shown in a previous paper<sup>1</sup> that, taking into account reactions (1), the following relationship holds between the mole fraction  $f_U$  and the monomer concentration [M] at which the polymer has been obtained:

$$f_U = \frac{2[M]}{2[M] + r_{77}} \times \frac{4[M]^2 + 2(r_5 + r_7 + r_{77})[M] + r_5 r_{77}}{4[M]^2 + 4(r_5 + r_7)[M] + r_5(r_5 + r_7)} \quad (2)$$

where  $r_5 = k_{C5}/k_p$ ,  $r_7 = k_{C7}/k_p$  and  $r_{77} = k_{C77}/k_p'$  are the cyclization ratios, representing a measure of the tendency of radicals  $M\cdot$ ,  $MM\cdot$  and  $C_7\cdot$  to react intramolecularly.

By introducing the experimental data of Table 1, into equation (2) one obtains, by a non-linear least squares method, the values of the cyclization ratios collected in Table 2. It is readily apparent that, independent of temperature, the formation during the polymer chain growth of both  $C_5\cdot$  and  $C_7\cdot$  radicals is decidedly more difficult

than the formation of  $C_7\cdot$  radicals, which has to be considered the main cyclization process. On the basis of the  $r_5$  and  $r_{77}$  values, one might conclude that reaction (1f) is less frequent than reaction (1a). It should however be pointed out that, owing to the form of equation (2), the evaluation of  $r_5$  and  $r_{77}$  when they are very small as compared with both  $r_7$  and [M], might suffer from some uncertainty. As a consequence, whilst it is possible to say with confidence that the inequalities  $k_{C5} \ll k_p$  and  $k_{C77} \ll k_p'$  hold, not too much significance must be attached to the numerical difference found for the values of  $r_5$  and  $r_{77}$ . For the same reason, it might be meaningless to try an interpretation of the quite ill-defined temperature dependence of these cyclization ratios. On the other hand, the change of  $r_7$  with temperature is as usual for cyclopolymerization processes, and seems worthy of detailed analysis.

By plotting the  $r_7$  values of Table 2 as a function of  $T$  according to the equation:

$$\ln r_7 = \frac{\Delta S_{C7}^\ddagger - \Delta S_p^\ddagger}{R} - \frac{E_{C7} - E_p}{RT}$$

where  $E_{C7}$  and  $E_p$  are the activation energies of reactions (1d) and (1e) respectively, and  $\Delta S_{C7}^\ddagger$  and  $\Delta S_p^\ddagger$  are the corresponding activation entropies, one obtains by the least squares method:

$$E_{C7} - E_p = 2.45 \pm 1.15 \text{ kcal/mol}$$

$$\Delta S_{C7}^\ddagger - \Delta S_p^\ddagger = 11.13 \pm 3.54 \text{ cal/K mol}$$

(1 cal = 4.1868 J), where the confidence limits are at the level of 95%.

The difference found between the activation energies is close to the values of 2.24 kcal/mol and 2.25 kcal/mol already reported for the analogous difference in the free radical cyclopolymerization of acrylic anhydride<sup>2</sup> and methacrylic anhydride<sup>3</sup>, respectively. This might be taken as an indication that the ring structure formed in reaction (1d) is not more highly strained than glutaric anhydride. The value found for  $E_{C7} - E_p$  is thus compatible with the formation of benzocycloheptene structures, which have been shown<sup>5</sup> to be practically free of strain.

As far as the difference  $\Delta S_{C7}^\ddagger - \Delta S_p^\ddagger$  is concerned, the value found on the basis of the experimental data of Table 2 must be compared with the value which can be calculated by a semiempirical method previously described<sup>1-3</sup>. Specifically, it has been reported<sup>1</sup> that for  $\Delta S_p^\ddagger$  one calculates:

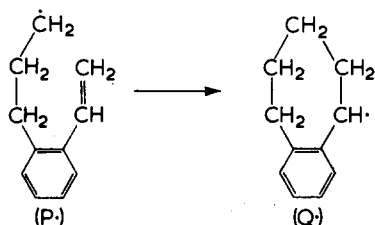
$$\Delta S_p^\ddagger = -28.25 \text{ cal/K mol}$$

For the evaluation of  $\Delta S_{C7}^\ddagger$  the assumption is made that the activation entropy of reaction (1d) is close to the en-

Table 2 Cyclization ratios of the free radical polymerization of *o*-DVB at different temperatures

Polymerization temperature (°C)	$r_5$ (mol/l)	$r_7$ (mol/l)	$r_{77}$ (mol/l)
70	0.08	7.59	0.03
60	0.08	6.39	0.03
50	0.25	5.94	~0
35	0.17	4.95	~0

ropy change of the following model reaction on the grounds that the entropy of the model product (Q·) is close to that of the transition state:



Therefore:

$$\Delta S_{C7}^{\ddagger} - \Delta S_p^{\ddagger} = S_{Q\cdot} - S_p$$

where  $S_p$  and  $S_{Q\cdot}$  are the molar entropies, at 298.16K in the ideal gas state, of P· and Q· radicals respectively which, as it has been already reported<sup>2</sup>, can be related to the molar entropies  $S_{PH}$  and  $S_{QH}$  of the parent compound PH and QH (namely, in the present case, *o*-propylstyrene and benzocycloheptene). The former can easily be obtained by adding to the molar entropy of *o*-methylstyrene (91.70 cal/K mol<sup>6</sup>) twice the contribution to entropy of a  $-\text{CH}_2-$  group, i.e. 9.37 cal/K mol (ref 2). Hence:

$$S_{PH} = 110.44 \text{ cal/K mol}$$

The molar entropy  $S_{QH}$  of benzocycloheptene can be estimated, like that of indan (benzocyclopentene)<sup>1</sup>, by applying a method similar to that by Bremner and Thomas<sup>7</sup>, according to the group equation:

$$S_{QH} = S_{\text{benzene}} + S_{\text{cycloheptane}} - S_{\text{ethane}} + R \ln \frac{(\sigma_{\text{benzene}})(\sigma_{\text{cycloheptane}})}{(\sigma_{\text{ethane}})(\sigma_{QH})} + 1.72 \quad (5)$$

where the  $S$  quantities are the molar entropies, at 298.16K in the ideal gas state, of the compounds indicated; the  $\sigma$ 's are the symmetry numbers of their molecules considered as rigid rotators ( $\sigma_{\text{benzene}} = 12$ ;  $\sigma_{\text{cycloheptane}} = 2$ ;  $\sigma_{\text{ethane}} = 6$ ;  $\sigma_{QH} = 2$ ), and the term 1.72 is the internal rotation contribution to the entropy of ethane<sup>8</sup>. Taking the molar entropies of ethane, benzene and cycloheptane from Stull, Westrum and Sinke<sup>6</sup>, one obtains from equation (5):

$$S_{QH} = 94.41 \text{ cal/K mol}$$

The difference  $S_{Q\cdot} - S_p$  can now be calculated on the basis of the relationship<sup>2</sup>:

$$S_{Q\cdot} - S_p = S_{QH} - S_{PH} + R \ln \frac{\sigma_{QH} \sigma_p}{\sigma_{Q\cdot} \sigma_{PH}}$$

where  $\sigma_{QH} = 2$ ,  $\sigma_p = 2$ ,  $\sigma_{Q\cdot} = 1$  and  $\sigma_{PH} = 3$  are the symmetry numbers of the molecular species indicated. Hence, on the basis of equation (4) one obtains:

$$\Delta S_{C7}^{\ddagger} = -15.46 \text{ cal/K mol}$$

and for the difference between the activation entropies of reactions (1d) and (1e) we calculate:

$$\Delta S_{C7}^{\ddagger} - \Delta S_p^{\ddagger} = 12.79 \text{ cal/K mol}$$

in excellent agreement with the experimental value. Such an agreement strongly supports the hypothesis that reaction (1d) yields a seven-membered ring structure. Moreover, as in previous cases<sup>2,3</sup>, the high tendency of MM· radicals to undergo reaction (1d) can be adequately understood on the basis of a smaller decrease in entropy in such a reaction, as compared with that of the intermolecular addition onto a monomer molecule, which compensates a slightly unfavourable situation from the point of view of the activation energies.

## REFERENCES

- 1 Costa, L., Chiantore, O. and Guaita, M. *Polymer* 1978, 19, 197
- 2 Guaita, M. *Makromol. Chem.* 1972, 157, 111
- 3 Chiantore, O., Camino, G., Chiorino, A. and Guaita, M. *Makromol. Chem.* 1977, 178, 125
- 4 Aso, C., Nawata, T. and Kamao, H. *Makromol. Chem.* 1963, 68, 1
- 5 Meier, H., Heiss, J., Suhr, H. and Müller, E. *Tetrahedron* 1968, 24, 2307
- 6 Stull, D. R., Westrum, E. F. and Sinke, G. C. 'The Chemical Thermodynamics of Organic Compounds', Wiley, New York, 1969, Ch. 9
- 7 Bremner, J. G. M. and Thomas, G. D. *Trans. Faraday Soc.* 1947, 43, 779
- 8 Herzberg, G. 'Infrared and Raman Spectra of Polyatomic Molecules', Van Nostrand, Princeton, 1945, Ch. 5