

Model study of the crosslinking of polydimethylsiloxanes by peroxides

Gaëlle Baquey, Laurence Moine, Odile Babot, Marie Degueil, Bernard Maillard*

Laboratoire de Chimie Organique et Organométallique, UMR 5802 CNRS, Université Bordeaux I, 351, cours de la Libération, 33405 Talence, Cedex, France

Received 13 January 2005; received in revised form 17 May 2005; accepted 17 May 2005

Available online 23 June 2005

Abstract

The decompositions of di-*t*-butyl peroxide (TBP) and diaroyl peroxides in permethylated silicone oil (47V20) have been studied by differential scanning calorimetry (DSC). Results show the importance of the solubility of the peroxide in the silicone on their rate of disappearance. For the diaroyl peroxides, according to the nature of the substituents on the phenyl ring and the concentration of the peroxide, the decomposition occurs in solution and/or in the solid phase. Decomposition in solution began at a lower temperature than in the solid phase, which took place immediately after melting and was quite instantaneous. Decomposition of these peroxides was also performed in octamethylcyclotetrasiloxane (D₄) and decamethyltetrasiloxane (DMTS). According to DSC results, D₄ seems to be a better model of the silicone than the linear one. Analyses of the products of the decomposition of TBP and dibenzoyl peroxide (BP) in this model showed that the dehydromer of D₄ was produced in low yield relative to peroxide. The main compounds obtained were high molecular weight compounds, which were apparently different for the two peroxides. The free radical origin of these products has been proven in the case of TBP by the addition of TEMPO in the reaction medium.

© 2005 Elsevier Ltd. All rights reserved.

Keywords: Polydimethylsiloxanes; Crosslinking; Peroxides

1. Introduction

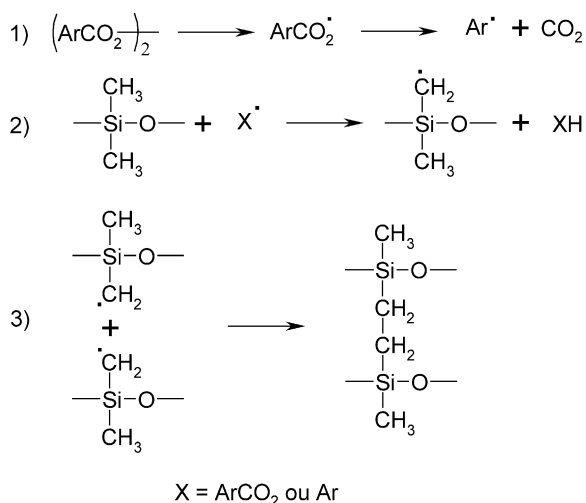
Polysiloxane or silicone productions have increased drastically since their discovery in the late 1940s because of their unique properties [1] as, e.g. thermal stability, electric insulation capacity, hydrophobic nature. Typically they are produced as linear macromolecules, which are later crosslinked to get elastomeric materials. Since the discovery of Wright and Oliver [2] in 1948, the main process to realize such a transformation involves the decomposition of peroxides in linear silicones. For this purpose, the most frequently used peroxides [(bis-2,4-dichlorobenzoyl peroxide (CIBP), BP, dicumyl peroxide, TBP and 2,5-dimethyl-2,5-bis-(*tert*-butylperoxy)hexane)] are classified in two families [3–5]: (i) ‘vinyl group specific catalysts’, (ii) ‘vinyl group non-specific catalysts’ [6]. The first class of peroxides is mainly constituted by the dialkyl ones which are unable to crosslink polydimethylsiloxanes (PDMS) if they do not contain some vinyl groups on the chain [7]. The

second class corresponds to the family of diaroyl peroxides because they can be used to crosslink PDMS whether vinyl groups are present or not [3,9].

Different mechanisms have been proposed to explain the ‘peroxidic’ crosslinking of the PDMS [[3,8–10] and references therein]. In particular, Loan [8] asserted that the crosslinking reaction must result from the abstraction of methyl hydrogen followed by the coupling of the polymeric radicals. Caprino [3] and Thomas [9] referred to the results of Kantor [11] on the decomposition of BP in D₄. A generally accepted mechanism of the dehydromerization of D₄ was proposed as a model reaction for the crosslinking of PDMS and is shown in Scheme 1.

Dluzneski [5] attributed the difference of reactivity of these two families to the inability of alkoxy radicals to abstract a hydrogen from a methyl of the PDMS for thermodynamic reasons. This is very surprising taking into account the energies of the generated and broken bonds cited here in. Moreover, considering the high efficiency of the alkoxy radicals to abstract a hydrogen atom [12,13], it is rather surprising to understand the inefficiency of dialkyl peroxide to crosslink the PDMS. This lack of knowledge on the free radical reactions involved in the peroxidic crosslinking of PDMS prompted us to study on the free

* Corresponding author. Tel.: +33 540 006445; fax: +33 540 006994.
E-mail address: b.maillard@lcoo.u-bordeaux1.fr (B. Maillard).



Scheme 1. Mechanism proposed for the crosslinking of polydimethylsiloxanes by a diaryl peroxide.

radical reactions occurring during the decomposition of these peroxides in models of PDMS. Preliminary results on this topic are reported herein.

The first part of the paper deals with a DSC analysis on the decomposition of several peroxides in various siloxane oil. Then, the thermolyses of one alkyl and one aroyl peroxides are performed in a model cyclosiloxane and the reaction products are analyzed.

2. Experimental part

2.1. Materials

D₄ was purchased from Lancaster, oil 47V20 from Prolabo, DMTS from Acros, TBP, BP and 2,2,5,5-tetramethylpiperidinyloxy (TEMPO) from Aldrich. Bis(-2,4-dichlorobenzoyl) peroxide (ClBP) was prepared according to a literature procedure [14]. 1-Methoxy 2,2,6,6-tetramethylpiperidine (MeTEMPO) [15] was prepared by heating a degassed solution of 4 mmol (0.53 g) of *t*-butyl peracetate [16] and 4 mmol (0.62 g) of TEMPO in benzene at 110 °C. After elimination of the solvent, the compound was purified by liquid–solid chromatography on alumina deactivated by w/w 6% water (elution by petroleum ether/chloroform 60/40) and isolated with a yield of 75%. (¹H NMR (250 MHz, CDCl₃, δ ppm): 3.53 (s, 3H, OCH₃), 1.50–0.91 (m, 18H, 3CH₂ of the piperidinic cycle and 4CH₃); ¹³C NMR (62.9 MHz, CDCl₃, δ ppm): 65.4 (C₁₀), 59.7 (C₁ and C₅), 39.6 (C₂ and C₄), 33 (C₆ and C₈), 19.9 (C₇ and C₉), 17 (C₃)).

2.2. Analytical techniques

Gas chromatography was performed on a Varian 3400 with a FID detector (detector temperature: 250 °C and

injector temperature 220 °C) fitted with a computer using the Star chromatography software. The apparatus was equipped with a CP–SIL 5CB column (30 m length, 0.25 mm inside diameter, 0.25 μm internal phase thickness, pressure 10 psi nitrogen gas carrier). It was used to identify (by comparison with standards) and to determine the amount of products arising from the thermal decomposition of the peroxy derivatives in D₄.

The thermal analyses of the siloxane/peroxy derivative mixtures were performed on a DSC 7 Perkin–Elmer apparatus running a Perkin–Elmer software. The experiments were run from 50 to 250 °C with a ramp of 2.5 °C/min. A known amount of peroxide was weighed in the stainless cap (with gold seal) and a precise volume of siloxane was poured on it to prepare the measure cap (the mixture was stirred before sealing the cap) meanwhile a similar empty stainless cap was used as the reference.

SEC analyses were performed with a double detection Waters apparatus (detectors Waters 410 (RI) and 486 (UV) and Waters 510 pump) equipped with TSK G2000HXL and G4000HXL columns in THF (1 ml/min) fitted with a computer running a Waters Millennium software.

NMR spectra (¹H, ¹³C and DEPT) were recorded with a Bruker AC 250 (250 MHz for ¹H and 62.9 MHz for ¹³C) and a DPX 300 apparatus (300 MHz for ¹H, 75.4 MHz for ¹³C and 59.6 MHz ²⁹Si INEPT). The solvent was CDCl₃ and chemical shifts are reported relative to tetramethylsilane; *J* values are quoted in Hz.

3. DSC study of the decomposition of peroxides in siloxanes

3.1. DSC study of the decomposition of the peroxides in 47V20

In order to study the decomposition of peroxides in PDMS, we have first performed these reactions in a DSC apparatus. This technique is well-adapted for qualitative studies of the decomposition of peroxides in various diluents [17]. The scanning of the thermal flow versus time under a constant rate of rising temperature leads to an exothermal phenomena resulting from the superposition of several processes: homolysis of the O–O bond generating free radicals and reactions (hydrogen abstraction, addition to unsaturations, scissions, coupling, disproportionation,...) of the various radicals produced in the medium [18].

TBP and BP have been chosen as representative examples of both classes of peroxides to be decomposed in silicone 47V20 (repetitive unit –O–Si(CH₃)₂–). Samples were prepared using 1 equiv. of peroxide for 40 methyl groups of the PDMS.

In Fig. 1(a), the thermogram given by TBP has a similar shape to the one usually obtained for the decomposition of a peroxide in solution [17,18]. Conversely, the curve obtained for the decomposition of BP in 47V20 is very different

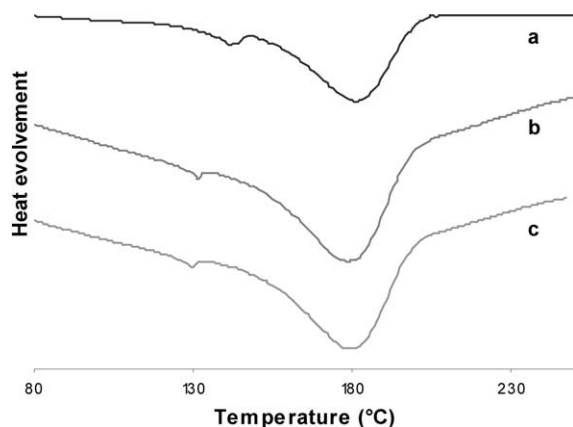


Fig. 1. DSC curves related to the decomposition of TBP (a) in silicone 47V20, (b) in D_4 and (c) in DMTS with a ratio peroxide/ $SiCH_3$ of 1/40.

(Fig. 2(a)). It might be attributed to the melting of the peroxide provoking its immediate decomposition due to the low solubility of BP in the silicone at room temperature. This was easily confirmed by the DSC analysis realized with the neat peroxide (Fig. 2(b)) and also by the observation of the reaction performed on a hot plate (carbon dioxide evolution with the melting of the solid showing the decomposition of BP). It is important to note for the reaction performed on the solid peroxide that there is a tail on the thermogram just after the melting-decomposition phenomena which is certainly due to the decomposition of small amount of BP dissolved in the previously generated decomposition products. Taking into account the manner of determination of the melting point of a solid by DSC [19], we equally decided to define the temperature of ‘melting-decomposition’ of the peroxide which might be a typical feature of the peroxide. Close values were obtained for the BP decomposed neat ($T_{\alpha} = 104.9\text{ °C}$) and in suspension in the silicone ($T_{\alpha} = 105.1\text{ °C}$).

In order to know the conditions of BP decomposition during the crosslinking of PDMS, we have operated with a much lower ratio of BP relative to the methyl groups of the silicone (1/1320 instead of 1/40), similar to the one

generally used in this polymer modification [20]. Fig. 2(c) presents the obtained thermogram showing that, in this case, complete decomposition of BP occurs in solution.

Due to the importance of CIBP in the crosslinking of silicones, we have decided to extend this DSC study to this peroxide (Fig. 2(f)–(h)). Comparison of the determined T_{α} in pure peroxide with the one realized in 47V20 (1/40) indicates that the decomposition occurred mainly in the solid state (respectively, 100.5 and 100.3 °C). For the more ‘dilute’ solution (1/1320), the shape of the thermogram seems to indicate the occurrence of peroxide decomposition in the solid state and in solution.

This preliminary study shows that the decomposition of both classes of peroxides in 47V20 is highly dependent of the solubility of the peroxide in the silicone and its intrinsic stability. Another important parameter for the diacyl peroxides is their melting point, in particular at high ratio of peroxide/methyl groups in the silicone, since the decomposition is driven only by the melting point of the solid for the neat peroxide.

3.2. Determination of a model of PDMS to study the decomposition of the peroxides by DSC

In order to identify the free radical reactions occurring in the course of the crosslinking of PDMS, we decided to design a low molecular weight model of this silicone. Among the commercially available siloxanes, we have selected D_4 and DMTS (Fig. 3). Taking into account the above results, a similar DSC study was performed with the three peroxides in these two models. First, one peroxide equivalent for 40 methyl groups of the siloxane was used.

As presented on the thermograms Fig. 1(b) and (c) a similar behavior of TBP in the three reactive diluents could be observed. Thus, D_4 and DMTS are acceptable models. Conversely, Fig. 2(a), (d) and (e) indicates that the decomposition of BP occurred differently in each diluent: in the solid state in the PDMS, in solution for DMTS and in both modes in D_4 . CIBP decomposes in the solid state in

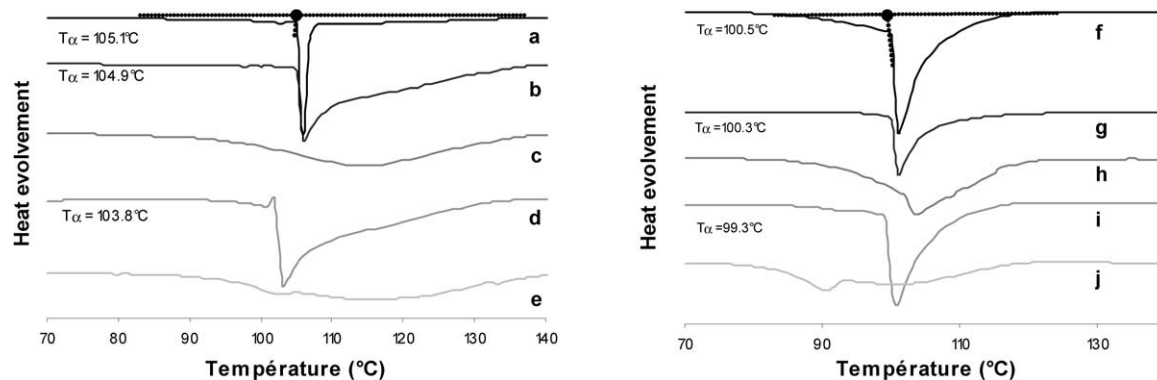


Fig. 2. DSC curves related to the decomposition of BP and CIBP in silicone 47V20, in D_4 and in DMTS (ratio peroxide/ $SiCH_3$) (a) BP in silicone 47V20 (1/40), (b) BP neat, (c) BP in silicone 47V20 (1/1320), (d) BP in D_4 , (e) BP in DMTS, (f) CIBP in silicone 47V20 (1/40), (g) CIBP neat, (h) CIBP in silicone 47V20 (1/1320), (i) CIBP in D_4 , (j) CIBP in DMTS.

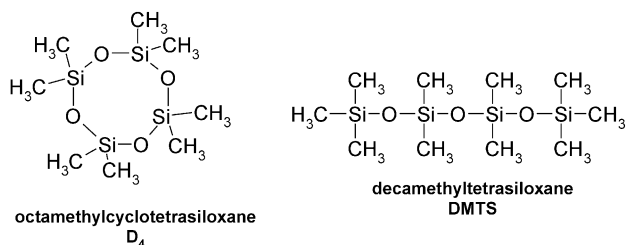


Fig. 3. Models of PDMS used in the current study.

47V20 and D_4 (Fig. 2(f) and (i)) and mainly in solution in DMTS (Fig. 2(j)). These experiments were completed by the study of the decomposition of BP and CIBP in D_4 with lower ratio peroxide/methyl of the siloxane (1/1320). The thermograms presented Fig. 4 show that the decomposition of BP occurs in solution in the silicone (Fig. 4(a)) and partly in solution and in the solid state in D_4 (Fig. 4(b)). For CIBP in D_4 , it occurs both in solution and in solid state and, in 47V20, mainly in solid state (Fig. 4(c) and (d)).

All these results of the DSC study on the decomposition of the peroxides in the three diluents are summarized Table 1. From the lecture of this table, we may consider that D_4 seems to be the best model of PDMS to perform a preliminary study of the free radical mechanisms which may occur during the decomposition of the peroxides in PDMS.

In conclusion, the DSC study of the decomposition of TBP and diacyl peroxides in 47V20 shows a great difference of solubility between these two types of peroxides. This difference influences drastically their decomposition pathways since the stability of the peroxides can be very different in solution and in the solid state. The comparative study of the decompositions of these peroxides in DMTS, D_4 and 47V20 indicates that the cyclic siloxane D_4 appears to be a better model than the short linear one to study the free

radical reactions that might occur in the course of the crosslinking of the PDMS by peroxides.

4. Study of the decomposition of TBP and BP in D_4

4.1. Decomposition of TBP in D_4

The thermolysis of TBP was performed at 165 °C, during 8 h with a relative amount of 1 mol of TBP for 5 moles of D_4 (molar ratio of 40 methyl per peroxidic function). Absence of the remaining TBP after reaction was verified by GC analyses and the presence of *t*-butanol, acetone and 2,2-dimethyloxirane were also detected. However, the GC titration of these compounds was difficult because of the reproducibility of the injections, caused in particular by their high volatility and by the dehydration of *t*-butanol. The presence of *t*-butanol indicates that *t*-butoxy radical is sufficiently reactive to abstract a hydrogen to a methyl of siloxane (Scheme 2). This result is in total opposition with the general affirmation of Dluzneski [5] and Dunham [7] of the inefficiency of this radical to react with siloxane. The small amounts of 2,2-dimethyloxirane (yield=2% relative to the TBP) are produced by the induced decomposition of TBP (Scheme 2) according to the proposal of Bell et al. [21]. However, such a reaction might be negligible compared to spontaneous decomposition of TBP. Formation of acetone arises from the fragmentation of *t*-butoxy radical which generates a methyl radical (Scheme 2).

Distillation of the crude reaction product led to the separation of the unchanged excess D_4 , a fraction containing mainly the dehydrodimer of D_4 (bis-heptamethylcyclotetrasiloxanyethane) produced with a yield of about 7% relative to TBP and a residue R1 (1.83 g from 20 mmol of decomposed TBP).

This residue R1 was studied by NMR and showed peaks for Si-CH₃ of cyclic siloxanes (¹H, $\delta=0.1$ ppm; ¹³C,

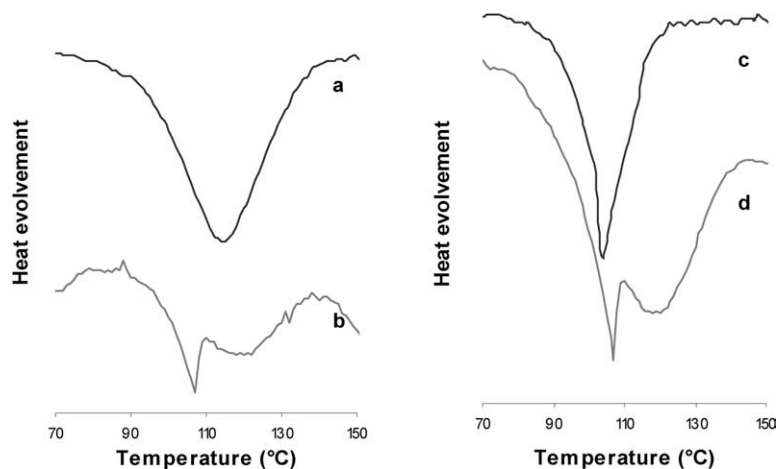


Fig. 4. DSC curves related to the decomposition of BP and CIBP in silicone 47V20, in D_4 with a ratio peroxide/SiCH₃ of 1/1320. (a) BP in silicone 47V20, (b) BP in D_4 , (c) CIBP in silicone 47V20, (d) CIBP in D_4 .

Table 1
Types of decomposition of peroxides in 47V20, D₄ and DMTS

Peroxide	47V20		D ₄		DMTS	
	1/40	1/1320	1/40	1/1320	1/40	1/1320
TBP	sol	sol	sol	sol	sol	sol
BP	M	sol	M+sol	sol	sol	sol
CIBP	M+sol	M+sol	M+sol	M+sol	sol	sol

M, melting-decomposition; sol, decomposition in solution.

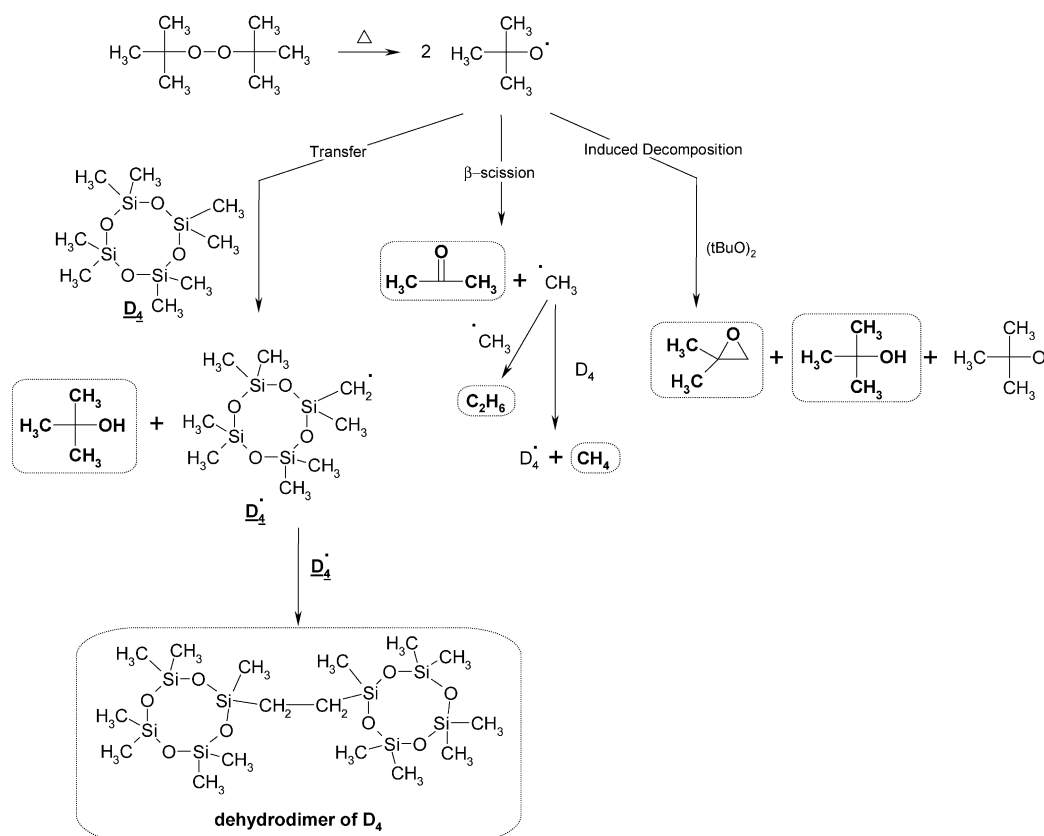
$\delta=0.15$ ppm; ^{29}Si , $\delta=-18.9$ ppm instead of -21.2 ppm for linear PDMS). In the ^1H NMR spectrum (Fig. 5), a broad signal around 2.2 ppm was observed and in the ^{13}C NMR one, a broad signal at 30 ppm, attributed by DEPT 135 to methine groups bearing probably to macromolecules. Integration of the protons of the methyl versus the methine ones gave roughly a value of 3 CH₃ for 1 CH.

Taking into account the hypothesis of a ‘polymeric’ structure of this residue, its SEC analysis indicated a monomodal distribution with a molar mass of about 1900 g/mol based on polystyrene equivalent.

Having only in hand the above elements, it appears difficult to identify the structure of this residue and, so, to propose a mechanism for its formation. In order to have more information about its formation, test reactions were performed in different conditions. First, D₄ was boiled at 165 °C. No oligomer was produced by this way so they may arise from a free radical process. To check this hypothesis,

TBP was decomposed in D₄ with 2 equiv. of TEMPO in order to trap the silylalkyl radicals as soon as they are formed. The GC analysis has shown the total disappearance of TBP and presence of TEMPO traces and of MeTEMPO (yield=17% relative to TBP) arising from the coupling of a methyl radical with TEMPO (Scheme 3). After elimination of excess D₄, a residue was obtained. Its ^1H NMR analysis indicated that it was constituted by 2,2,6,6-tetramethylpiperidinyloxymethylheptamethylcyclotetrasiloxane (D₄-TEMPO) (yield=81% relative to TBP) generated by trapping of D₄· radicals by TEMPO (Scheme 3). Considering the yields of formation of these two adducts, 98% of radicals generated by TBP are trapped by TEMPO. This observation and absence of formation of dehydromer of D₄ and of high molecular weight products are consistent with the free radical origin of the residue involving D₄· radicals when reaction is performed without TEMPO.

To understand the reactivity of *t*-butoxy radicals, it seems



Scheme 2. Mechanisms of formation of the TBP decomposition products in D₄.

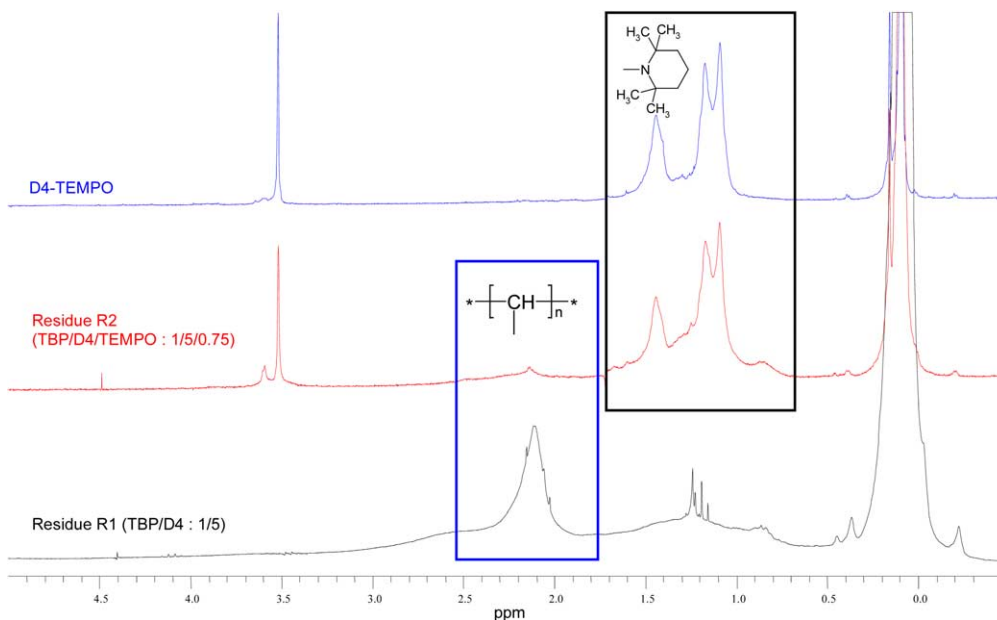
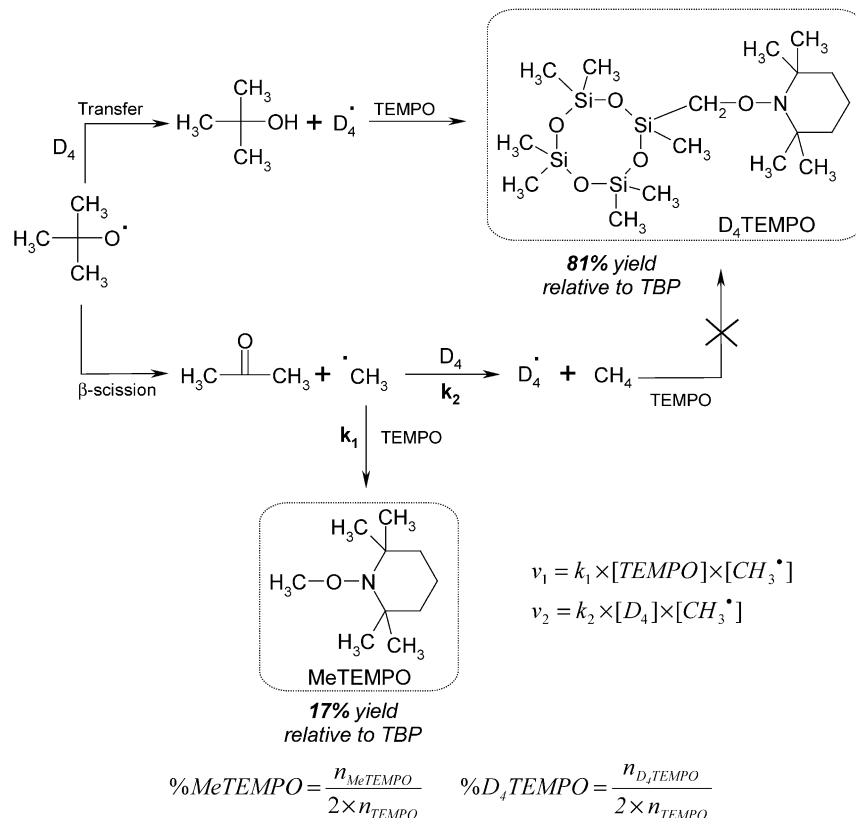


Fig. 5. Comparison of ^1H NMR spectrum of D_4TEMPO and R1 and R2 residues.

necessary to determine the ratio of the rates of transfer and β -scission (r_{ts}) for the $t\text{BuO}\cdot$ radicals in D_4 solution. Such a determination is not possible from the ratio of formed $t\text{BuOH}$ versus acetone because of the GC titration difficulties of these products. So r_{ts} was calculated from the ratio of $\text{D}_4\text{-TEMPO}$ and MeTEMPO . Indeed, the high

percentage (98%) of trapped radicals relative to decomposed TBP in presence of TEMPO and the kinetic analysis of their formation mechanism may allow us to determine this ratio r_{ts} . We have to take into account that the D_4TEMPO is formed by radicals coupling of TEMPO and $\text{D}_4\cdot$ radicals arising from hydrogen abstraction to a methyl group of D_4 by



Scheme 3. Mechanisms of formation of the products in the decomposition of TBP in D_4 and in the presence of TEMPO.

t-butoxy or by methyl radicals. As seen Scheme 3, $\text{CH}_3\cdot$ radicals could be involved in two reactions: (i) coupling with TEMPO leading to the formation of MeTEMPO (Scheme 3, $\nu_1 = k_1[\text{TEMPO}][\text{CH}_3\cdot]$ with $k_1 \sim 10^7 \text{ mol}^{-1} \text{ s}^{-1}$ [22,23]), (ii) hydrogen abstraction to D_4 leading to $\text{D}_4\cdot$ radicals (Scheme 3, $\nu_2 = k_2[\text{D}_4][\text{CH}_3\cdot]$ with $k_2 \sim 10^2 \text{ mol}^{-1} \text{ s}^{-1}$ [22,23]). Such a hydrogen abstraction is negligible if $\nu_1/\nu_2 = k_1[\text{TEMPO}]/k_2[\text{D}_4] > 10$, so if $[\text{TEMPO}]/[\text{D}_4] > 10^{-4}$. In the reaction conditions used, the molar ratio TEMPO/ D_4 is higher than 10^{-4} during the course of the reaction, the initial ratio being 0.4. Therefore, formation of $\text{D}_4\cdot$ -TEMPO can only be attributed to the coupling of TEMPO and $\text{D}_4\cdot$ radicals arising from a hydrogen abstraction by *t*BuO \cdot radicals. Thus, a value of 4.8 for ratio r_{ts} of the rate constant of transfer and fragmentation was calculated. Such a value indicates that *t*BuO \cdot radicals react via by hydrogen abstraction rather than by fragmentation. These results confirm that *t*BuO \cdot radicals arising from TBP decomposition are able to abstract efficiently a hydrogen of a Si- CH_3 group. So, the hypothesis of Dlużneski [5] and Dunham [7] is not realistic.

The reaction performed in presence of TEMPO shows the efficient production of $\text{D}_4\cdot$ radicals resulting from the hydrogen abstraction from D_4 by *t*-butoxy radicals. It is, therefore, very surprising that in absence of TEMPO, very small quantities of the dehydrodimer were isolated. It would indicate that the dimerization of the radicals is not efficient and/or that these radicals would prefer to react by another pathway to produce high molecular weight products. Another explanation could be forwarded considering the dimer as the main source of polymer formation. The rate constants of the termination reactions involving two primary alkyl radicals [24] indicate that there is no apparent reason for the blocking of the dimerization of the silylmethyl radicals. Concerning the consumption of the dimer by radical reactions, one can imagine reactive sequence shown in Scheme 4.

Formation of the high molecular weight products might be attributed to the abstraction of a hydrogen from a methylene having a higher reactivity towards *t*-butoxy radicals than the one of a methyl, but also from the numerous methyl present in the dehydrodimer. Whatever the type of compound, it could in principle be obtained from the dehydrodimer radical by coupling with an other dehydrodimer radical or with a $\text{D}_4\cdot$ radical. However, from ^1H NMR spectrum of the residue, it was not possible to find compounds having a ratio of 1 CH for 3 CH_3 . Difficulties to identify the structure of the 'polymeric' residue do not allow us to propose a mechanism explaining the formation of the high molecular weight products. Despite the fact that D_4 is an acceptable model of PDMS on the basis of the DSC study, it appears necessary to replace it by a model of lower molecular weight and of simpler structure. This substitute should allow us to analyze more deeply products of reaction and, so, to understand the mechanism of the reaction leading to the generation of the high molecular weight products.

4.2. Decomposition of BP in D_4

Despite the difficulty in identification of products resulting from the decomposition of TBP in D_4 , we have decided to perform the same reaction replacing TBP by BP. It was expected to see first a difference in the yields of the dehydrodimer formation and second absence or presence of the same type of residue as with TBP. This study should allow us to determine the difference of behavior between the two classes of peroxide.

Decomposition of BP in D_4 was performed by heating the compounds at 130 °C during 6 h with a relative ratio of BP to D_4 of 1/5 (1 peroxide function for 40 methyl groups). Conversely to TBP, it was impossible to determine by GC if the peroxide was totally decomposed, due to its decomposition in GC injector. However, taking into account the time of reaction and the rate constant of decomposition of BP in similar solvents [25], it is a fair assumption that there was no remaining peroxide.

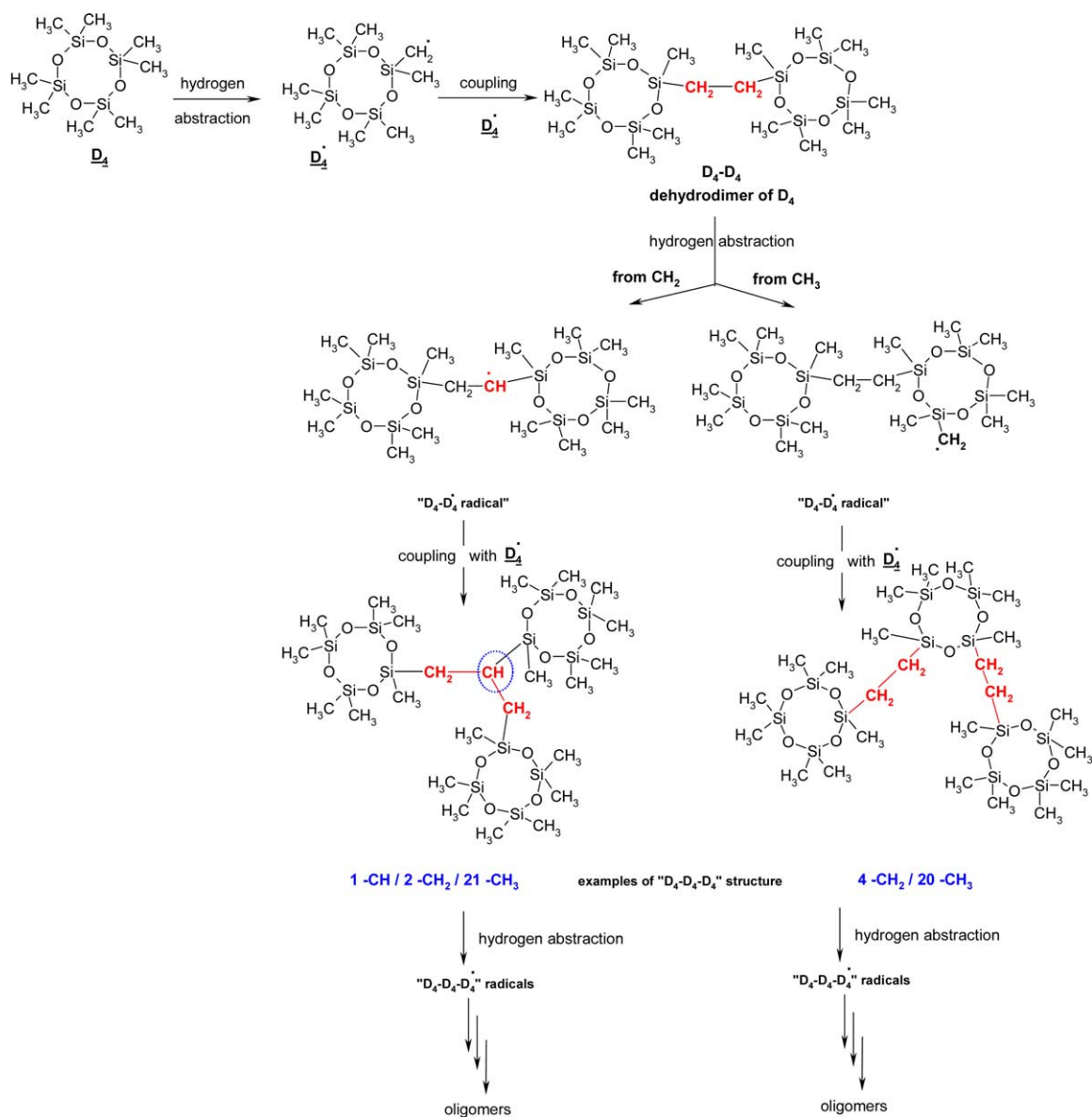
Various compounds arising only from BP were identified and titrated by GC. Table 2 summarizes these results and Scheme 5 presents their mechanism of formation. Benzoic acid was formed, as proven by isolation after extraction by an aqueous sodium hydroxide solution followed by acidic regeneration, with a yield of 13% relative to the starting BP. The relative amount of benzoic acid and benzene shows that benzoyloxy radicals are not enough reactive towards the hydrogens of D_4 to prohibit their decarboxylation.

The dehydrodimer of D_4 was produced with a yield of 11% relative to BP. After distillation of excess D_4 and of decomposition compounds, a residue was isolated (2.8 g for 20 mmol of BP decomposed) and analyzed by SEC. A bimodal distribution of high molecular products was obtained with respective molar masses of 700 and 1800 g/mol polystyrene equivalent.

A test reaction, realized by heating D_4 in presence of benzoic acid, has proven that the residue could not be attributed to a degradation of D_4 in the course of the reaction.

NMR analyses of the residue showed the presence of several entities: (i) aromatic protons of Ph and PhCO_2 entities (^1H NMR, 7–8.2 ppm and ^{13}C NMR, 120–134 ppm) (ii) SiCH_3 of a cyclic siloxane (^{29}Si NMR, –18.9 ppm instead of –21.2 ppm for a linear PDMS). Here, it is important to note that no methine proton has been observed in the NMR spectrum of the residue unlike in the case of the reaction performed with TBP.

Assuming that the residue is essentially constituted by aromatic entities (Ph and/or PhCO_2) and D_4 ones, combination of the integration of the ^1H NMR of the residue (about 50 methyl for 1 aromatic group) with its produced mass allows to estimate a yield of 4% of incorporation of aromatic entities from the starting BP (Table 2). The balance of aromatic entities identified in the various products (Table 2) shows that around 25% relative to the starting peroxide is missing. This can be attributed to several possibilities:

Scheme 4. Mechanism of the production of high molecular weight compounds from the dehydromer of D_4 .

- the way of titration of benzoic acid which introduce certainly an important incertitude
- the presence of numerous unidentified products present in very small amounts.
- the approximations in the estimation of the aromatic moieties present in the residue.

The induced decomposition of BP by TEMPO [26]

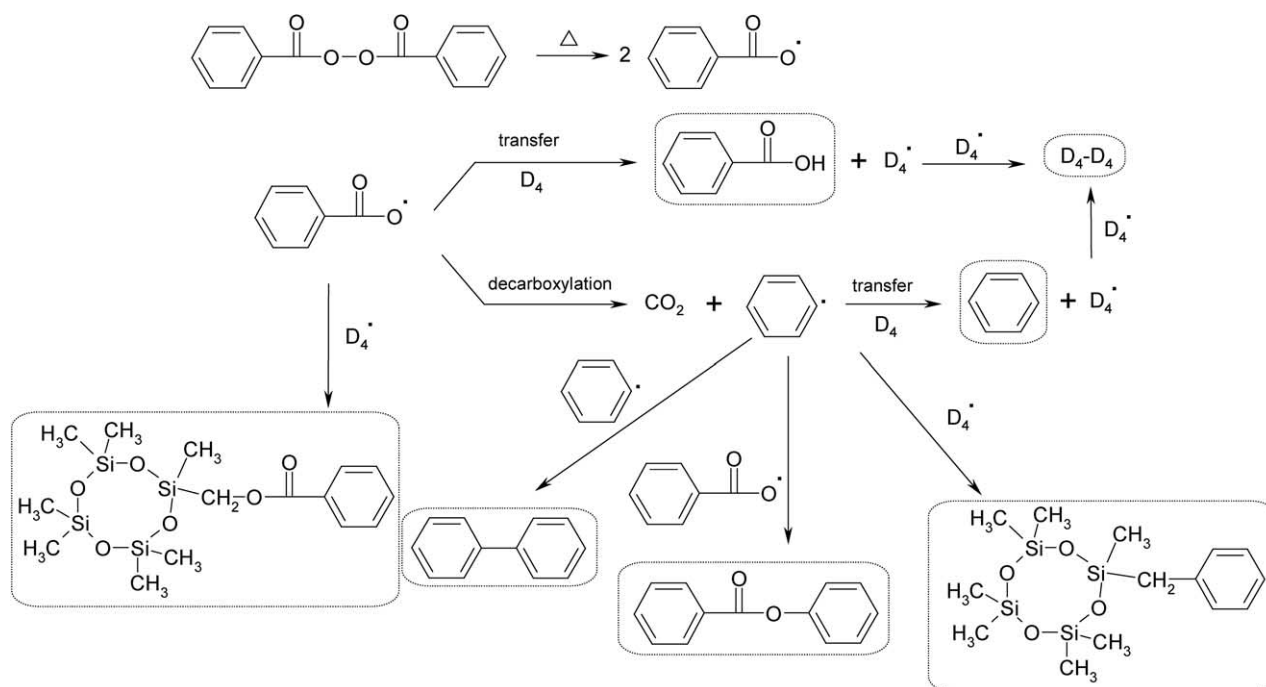
Table 2
Products of decomposition of BP in D_4

	Ph-H	PhCO ₂ H	PhCO ₂ Ph	Ph-Ph	Residue	Total
Balance of aromatics groups (relative to starting BP)	53%	13%	5%	2%	4%	77%

prohibited the use of this compound to check the possible free radical origin of this residue.

5. Conclusion

The DSC study of the decompositions of TBP and diaryl peroxides in 47V20 shows very different behaviour:

Scheme 5. Mechanisms of formation of the products in the decomposition of BP in D_4 .

- TBP is totally soluble in the silicone and so it decomposes in solution.
- Diaroyl peroxides can decompose in solution or in the solid state depending on the nature of the peroxide and its concentration. The decomposition in the solid state begins at higher temperature than in solution but it is immediate as soon as the peroxide melts. Nevertheless, in the domain of concentration used for the crosslinking, the main decomposition would occur in solution, except for CIBP.

The DSC study of the behavior of the three peroxides in D_4 , DMTS and 47V20 prompted the choice of D_4 as a model of PDMS to study their decomposition in order to try to identify the free radical reactions occurring in silicones.

Analysis of the products formed in the decomposition of TBP and BP in D_4 shows that the free radicals arising from the homolysis of the peroxide generate silylalkyl radicals by abstraction of a hydrogen from D_4 . These radicals can combine to produce the dehydrodimer as pointed out by Kantor [11]. Nevertheless, the yield of formation of this dehydrodimer relative to the peroxide is very low (about 10%). In both decompositions, a great part of the produced material is constituted by high molecular weight compounds which, according to NMR, are different according to the peroxide involved.

Taking into account the above results, in particular the relatively low yields of the formation of the dehydrodimer of D_4 , it is difficult at the moment to reach the same conclusion than Loan [8] on the mechanism of the crosslinking of PDMS. A deeper study allowing the

knowledge of the structures of the products present in the residues will be necessary to know their mechanism(s) of formation before proposing an alternative to the admitted mechanism. So, despite the results obtained by DSC leading to the choice of D_4 as the best model for PDMS, the determination of the free radical reactions occurring during the silicone crosslinking will be approached by studying the decomposition of the above peroxides in hexamethyldisiloxane because of its single site attack on the methyl and its low molecular weight, even if we cannot consider it as a model of PDMS, whose repetitive unit is $[-OSi(Me)_2O-]$.

Acknowledgements

The authors acknowledge Akzo Nobel for a fellowship (2001–2004) to one of us (G. Baquey), Drs J. Meijer, J. Jelenic and L. Vertommen (Akzo Nobel) for very fruitful discussions during the course of this study.

References

- [1] Les silicones, Production et Application, Rhône-Poulenc Département Silicones, Techno-Nathan; 1988.
- [2] Wright JGE, Oliver SG, US Patent 2.448.565; 1948.
- [3] Caprino JC, Macander RF. In: Rubber technology. 3rd ed. New York: Reinhold; 1987. p. 375.
- [4] Nijhof L, Cubera M. Rubber Chem Technol 2001;74:181.
- [5] Dluzneski PR. Rubber Chem Technol 2001;74:451.
- [6] The first comment to do on this classification is related to the inappropriate use of the word 'catalyst'. Indeed, we have to underline that a catalyst is a compound participating to the reaction in order to

- accelerate it, but recovered unchanged at the end. As peroxides are decomposed in the course of the reaction, in the proposed classification the term 'catalyst' must be replaced by the term 'peroxide'.
- [7] Dunham ML, Bailey DL, Mixer RY. *Ind Eng Chem* 1957;49:1373.
- [8] Loan LD. *Rubber Chem Technol* 1967;40:149.
- [9] Thomas DR. Siloxane polymers. In: Clarson SJ, Semlyen JA, editors.. New Jersey: Prentice Hall; 1993. p. 567.
- [10] Brooke MR. In: Silicon in organic, organometallic and polymer chemistry. New York: Wiley; 2000. p. 282.
- [11] Kantor SW, 130th Meeting Am Chem Soc; 1956.
- [12] Howard JA. Radical reaction rates in liquids, in Landolt–Börnstein: numerical data and functional relationship in science and technology, new series. vol. 13d. Berlin: Springer; 1984. p. 38.
- [13] Kochi JK. In: Kochi JK, editor. Free radicals, vol. 2. New York: Wiley; 1973. p. 690.
- [14] Prices CC, Krebs E. *Org Synth* 1943;23:65.
- [15] Ciriano MV, Korth HG, van Scheppingen WB, Mulder P. *J Am Chem Soc* 1999;121:6375.
- [16] Bartlett PD, Hiatt RR. *J Am Chem Soc* 1958;80:1398.
- [17] Navarro C, Saux A, Vertommen L, Maillard B. *New J Chem* 1992;16:987.
- [18] Filliatre C, Maillard B, Villenave JJ. *Thermochim Acta* 1979;30:83.
- [19] Wendtland WWM. *Thermal analysis*. 3rd ed. New York: Wiley; 1986. p. 410.
- [20] Jelenic J, private communication, Akzo Nobel; 2001.
- [21] Bell ER, Rust FF, Vaughan WE. *J Am Chem Soc* 1950;72:337.
- [22] Chateaneuf J, Lusztyk J, Ingold KU. *J Org Chem* 1988;53:1629.
- [23] Fossey J, Lefort D, Sorba J. *Les radicaux libres en chimie organique*. Paris: Masson; 1993.
- [24] Ingold KU. In: Kochi JK, editor. Free radicals, vol. 1. New York: Wiley; 1973. p. 37.
- [25] Masson JC. In: Brandrup J, Immergut EH, editors. *Polymer handbook*. New York: Wiley; 1989. p. II-31.
- [26] Wang D, Wu Z. *Macromolecules* 1998;31:6727.