

THERMAL AND DYNAMIC MECHANICAL INVESTIGATIONS ON POLY[BIS(BENZIMIDAZOBENZISOQUINOLINONES)]

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ABSTRACT

A series of new semi-ladder poly[bis(benzimidazobenzisoquinolinones)], obtained by the polycondensation of dinaphthalene dianhydrides and aromatic tetraamines was investigated by TG, DSC and DMA methods. The influence of polymer structure on the thermal behaviour of the poly[bis(benzimidazobenzisoquinolinones)] was examined. The polymers were found to be thermally stable with $T_d > 723$ K in air and T_g ranging from 585 to 701 K. A good agreement was obtained in T_g values measured by DSC and DMA methods. It was found that some cross-linking processes occurred at temperatures above T_g . Some of the isothermal ageing curves were used to find the activation energies of isothermal cross-linking and decomposition.

INTRODUCTION

In previous papers [1–3] we reported on the synthesis of a new group of thermally stable semi-ladder heterocyclic polymers, namely the poly[bis(benzimidazobenzisoquinolinones)], obtained by the one-step high-temperature solution polycondensation of dinaphthalene dianhydrides with aromatic tetraamines. These works have led to the preparation of a series of high molecular mass polymers soluble not only in strong acids, but also in organic solvents [2,3], which allowed tough films to be obtained from most of them. Owing to the fact that thermal properties are of prime importance in processing and application, the thermal and thermomechanical behaviour of these polymers was studied, the structural effects also being taken into account. The results of the above studies are presented in this paper.

EXPERIMENTAL

Poly[bis(benzimidazobenzisoquinolinones)] were synthesized from the following dianhydrides: 4,4'-(phenylene-1,3-dioxy)dinaphthalene-1,8:1',8'-te-

tricarboxylic, 4,4'-(naphthalene-2,7-dioxy)dinaphthalene-1,8 : 1',8'-tetracarboxylic, 4,4'-(biphenylene-2,2'-dioxy)dinaphthalene-1,8 : 1',8'-tetracarboxylic, 4,4'-[sulphidylbis(*p*-phenyleneoxy)]dinaphthalene-1,8 : 1',8'-tetracarboxylic, 4,4'-[sulphonylbis(*p*-phenyleneoxy)]dinaphthalene-1,8 : 1',8'-tetracarboxylic, 4,4'-[carbonylbis(*p*-phenyleneoxy)]dinaphthalene-1,8 : 1',8'-tetracarboxylic, 4,4'-[isopropylidenebis(*p*-phenyleneoxy)]dinaphthalene-1,8 : 1',8'-tetracarboxylic, 4,4'-[benzhydrylidenebis(*p*-phenyleneoxy)]dinaphthalene-1,8 : 1',8'-tetracarboxylic, 4,4'-[fluorenylidenebis(*p*-phenyleneoxy)]dinaphthalene-1,8 : 1',8'-tetracarboxylic, 4,4'-[10-oxo-9,10-dihydroanthrylidenebis(*p*-phenyleneoxy)]dinaphthalene-1,8 : 1',8'-tetracarboxylic and 3,3'-diaminobenzidine (polymers **I**, **III–V**, **VII**, **IX**, **X**, **XII**, **XIII**, **XV**) and from the above-mentioned dianhydrides and 3,3',4,4'-tetraaminodiphenyl ether (polymers **II**, **VI**, **VIII**, **XI**, **XIV**). The general procedure for their preparation is given in ref. 4.

Viscosity measurements

These were carried out in 0.5% (w/v) solutions of polymers in a tetrachloroethane–phenol mixture (3 : 1) at 298 K, using an Ubbelohde's suspended-level viscometer.

Thermal behaviour

Dynamic thermogravimetric (TG) analysis was performed on a derivatograph (MOM, Budapest) operating at a heating rate of 10 K min⁻¹ in air and in argon.

Thermograms of isothermal weight losses for kinetic studies were obtained using the Setaram thermobalance system including the model B 60 balance and the Setaram furnace (1600°C). At the same time a Setaram time derivative computer was used to find the rate of weight changes. The temperature was programmed and controlled by means of a temperature programmer (PT 3000) and temperature regulator (RT 3000) with a Pt/Pt–10%Rh thermocouple.

Isothermal ageing of polymer samples at 553 K was carried out in air in a specially designed ageing oven, the weight losses being measured during a period of 30 days.

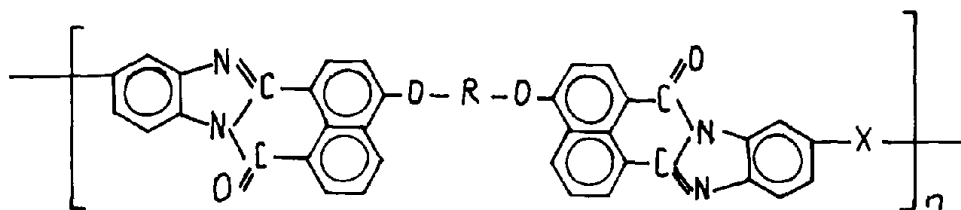
A DuPont Model 990 thermoanalyzer was used to find the glass transition temperature values (heating rate 20 K min⁻¹, nitrogen atmosphere).

Dynamic mechanical analysis

Storage modulus, E' , and loss tangent were determined by using a Rheovibron viscoelastometer (Model DDV-I-B, frequency 3.5 Hz, heating rate 2 K min⁻¹, film thickness 20–50 μm, nitrogen atmosphere).

RESULTS AND DISCUSSION

The subject of this investigation is poly[bis(benzimidazobenzisoquinolinones)] described by the following formula



where R and X have the meanings given in Table 1. Molecular masses (η_{red} , cf. Table 1) and the solubility of these polymers in a tetrachloroethane-phenol (3:1) mixture (polymers I, II, V, VI, VII, VIII, X, XI, XIII, XIV) made it possible to cast polymer films from their 5–7% solutions.

Thermal behaviour

Dynamic thermogravimetric analysis showed a high thermal and thermo-oxidative resistance of the poly[bis(benzimidazobenzisoquinolinones)] obtained. Their initial decomposition temperatures were, in all cases, higher than 723 K and did not depend on the atmosphere applied, i.e., air or argon. For a given polymer, the T_d values recorded in air and argon were similar, which would suggest that the decomposition process was not initiated by oxygen (Table 2, Fig. 1).

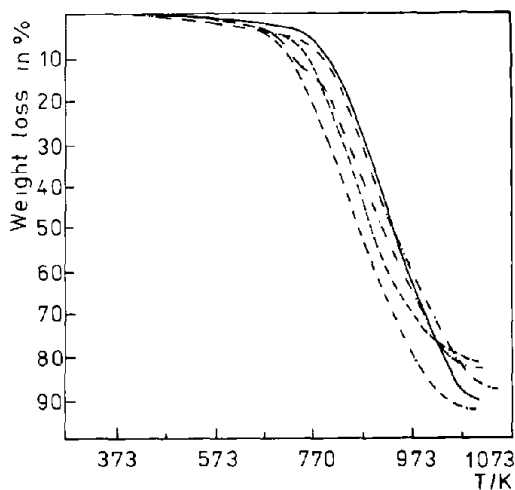



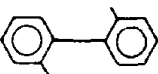
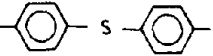
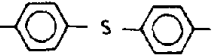
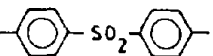
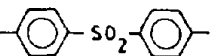
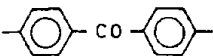
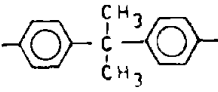
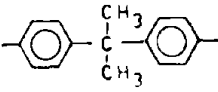
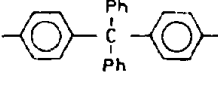
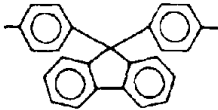
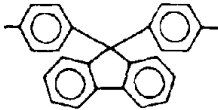
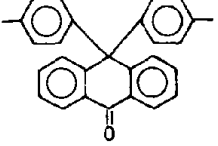


Fig. 1. Examples of TG curves obtained for poly[bis(benzimidazobenzisoquinolinones)] in air (heating rate = 10 K min⁻¹): (· · · · ·) polymer I; (- - - - -) polymer V; (- · · · ·) polymer VII; (- - - - -) polymer X; (—) polymer XIII.

TABLE 1

Structures and reduced viscosities of poly[bis(benzimidazobenzisoquinolinones)]

Polymer No.	R	X	η_{red} (dl g ⁻¹) ^a
I		—	3.95 ^b
II		—O—	1.18 ^b
III		—	1.53
IV		—	0.20
V		—	1.89 ^b
VI		—O—	1.59 ^b
VII		—	1.00 ^b
VIII		—O—	0.97 ^b
IX		—	0.96
X		—	1.00 ^b
XI		—O—	0.95 ^b
XII		—	0.32
XIII		—	1.03 ^b
XIV		—O—	0.84 ^b
XV		—	0.47

^a Measured in a 3:1 tetrachloroethane-phenol mixture.^b Polymers giving tough, transparent films.

The decomposition temperatures of various polymers were different and structure dependent. The highest T_d values were found for polymers I, II, IX, XIII and XIV, i.e., for those containing the smallest number of heteroatoms

TABLE 2

Thermal properties of poly[bis(benzimidazobenzisoquinolinones)]

Polymer No.	T_g^a (K)	T_g^b (K)	T_d^c in argon (K)	T_d^c in air (K)	$T_{d,max}^c$ in air (K)	Weight loss (%) at ^c		
						673 K	873 K	1073 K
I	668	671	793	793	873	2	25	85
II	641	644	783	783	863	2	40	84
III	686	—	793	783	853	5	22	65
IV	649	—	773	773	873	2	15	82
V	658	660	763	763	863	2	18	67
VI	612	626	763	763	863	2	27	76
VII	677	699	743	743	773	3	24	75
VIII	633	661	733	733	763	2	25	84
IX	662	—	793	773	873	4	20	85
X	646	660	743	733	833	4	28	80
XI	585	629	723	713	813	3	39	87
XII	630	—	773	773	873	3	20	87
XIII	694	—	793	793	873	3	30	87
XIV	659	679	793	793	853	2	20	74
XV	701	—	763	743	873	3	34	85

^a Determined by DSC.^b Determined by DMA.^c Based on TG data, heating rate 10 K min⁻¹.

or aliphatic groups as linking bridges in the polymer chain. The kind of aromatic groups present in the dioxyarylene fragments of polymer chains was less significant. There were no significant differences between the T_d values of polymers with 1,3-phenylenedioxy, 2,7-naphthalenedioxy, or 9,9-fluorenylidenebis(*p*-phenyleneoxy) ring systems. The introduction of sulphide, sulphone or isopropylidene linkages into the polymer chain lowered the T_d values in the following order: $-S-> -SO_2-> -C(CH_3)_2-$. The replacement of 3,3'-diaminobenzidine with 3,3',4,4'-tetraaminodiphenyl ether resulted in a decrease in the decomposition temperature by some 10–20 K.

In order to examine the thermal stability of poly[bis(benzimidazobenzisoquinolinones)] in all aspects, these polymers were also submitted to long-term annealing at 573 K for a period of one month. All these structure–property relationships found as a result of dynamic TG analysis were confirmed by those of the isothermal analysis (cf. Table 3, Fig. 2). The lowest weight losses were observed for polymer I with 1,3-phenylenedioxy linkages, while the highest weight losses were found for polymer XI containing aliphatic bridges.

DSC analysis showed that all the synthesized poly[bis(benzimidazobenzisoquinolinones)] had glass transition temperatures, T_g , below their decom-

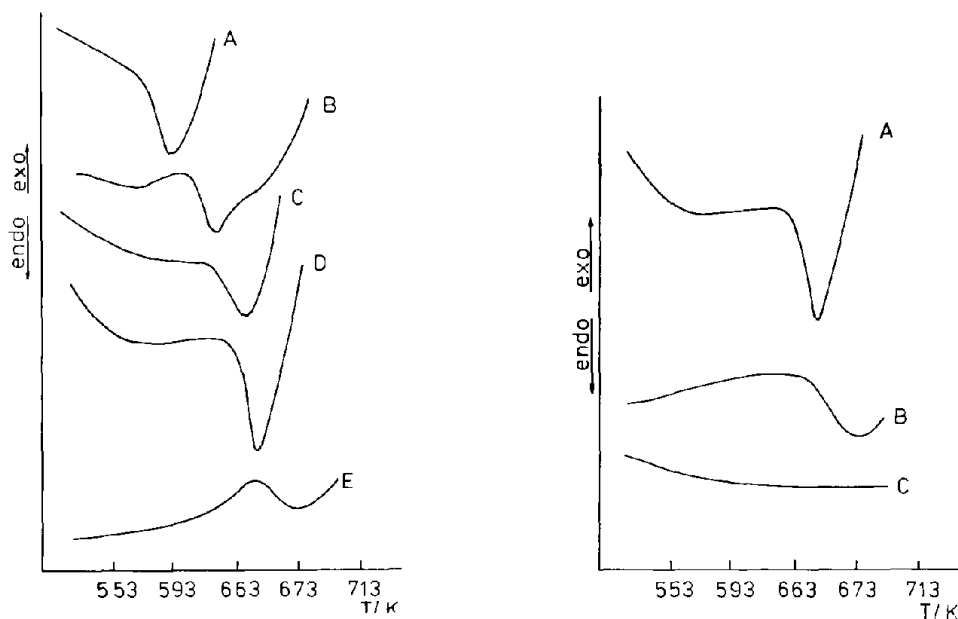


Fig. 2. DSC curves of the poly[bis(benzimidazobenzisoquinolinones)] (heating rate = 20 K min^{-1} , nitrogen atmosphere): (A) polymer XI; (B) polymer VI; (C) polymer VIII; (D) polymer II; (E) polymer XIV.

Fig. 3. DSC recorder traces of poly[bis(benzimidazobenzisoquinolinone)] II: (A) heated to 673 K; (B) after annealing at 673 K for 1 h; (C) after annealing at 673 K for 3 h.

TABLE 3
 Isothermal ageing of the poly[bis(benzimidazobenzisoquinolones)] at 553 K in air

Time of anneal- ing (days)	Weight loss of polymers (%)													
	I	II	V	VI	VII	VIII	X	XI	XIII	XIV				
5	2.3	2.5	2.0	2.6	3.0	3.5	9.0	12.9	2.9	3.0				
10	2.5	2.6	2.2	2.7	3.7	10.0	20.1	27.8	6.8	6.8				
15	4.3	7.2	3.8	3.9	12.5	28.8	34.3	42.4	14.2	14.3				
20	6.8	12.6	11.6	16.9	27.0	43.4	44.5	52.4	16.6	23.8				
25	9.2	18.4	20.5	27.6	36.5	51.3	50.7	57.2	22.9	30.7				
30	13.5	26.8	33.2	45.0	52.0	60.8	58.2	63.3	32.2	42.3				

position temperatures, T_d . The phase transitions took place in the temperature range 585–701 K (cf. Table 2). The T_g values were structure dependent, the kind and amount of flexible linkages in the repeating-chain unit being the decisive factor. The introduction of each additional ether linkage into the repeating unit (introduced using tetraamine as a monomer containing such a linkage) involved, in all cases, a decrease in T_g , as high as 60 K in some cases (polymers X, XI). Examples of the DSC curves obtained (polymers II, VI, VIII, XI, XIV) are presented in Fig. 2.

All the DSC curves exhibit a broad endotherm at ~ 373 K during the first run, which was assigned to the presence of water in the polymer chain. These signals did not appear in the second run, which indicated the physical nature of the sorption. Except for these endotherms, no other heat effects were to be observed until the respective glass transition temperatures had been reached. However, a strong exothermic effect was present above the glass transition temperature. In order to determine whether this exothermic effect is due to polymer destruction or to some secondary reactions leading to the formation of cross-linked structures, polymer II was subjected to repeated DSC analyses. A sample was heated to 673 K in an inert atmosphere, then cooled, and recordings were made at a heating rate of 20 K min^{-1} . After the first and second runs to 673 K the sample was additionally annealed at 673 K for 1 and 3 h, respectively. The DSC scans obtained are given in Fig. 3. It was noted that the glassy peaks were shifted to higher temperatures with increasing annealing time. At the same time, these peaks decreased gradually in size and then disappeared completely.

A more detailed study on the kinetics of decomposition of one of the synthesized poly[bis(benzimidazobenzisoquinolinones)] (polymer I) derived by isothermal weight loss tests in nitrogen at 753, 763, 773 and 783 K (Fig. 4) made it possible to gain some information about activation energies of decomposition.

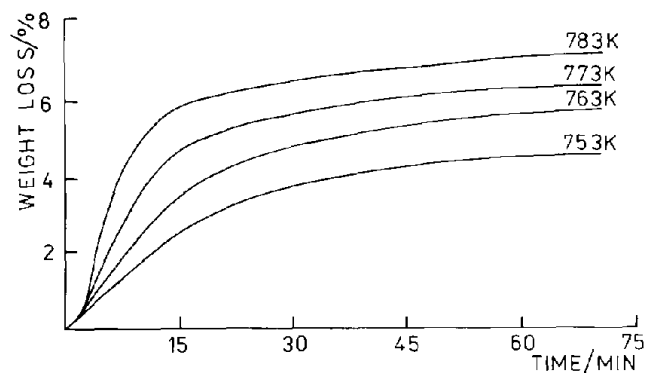


Fig. 4. Weight losses of polymer I due to isothermal exposure to various temperatures (determined using the Setaram thermobalance system in nitrogen).

The value of the activation energy, E_a , was calculated from the slope of the straight-line dependence between the logarithm of the maximum decomposition rate and the inverse temperature [5]. It was found to be 212 kJ mol^{-1} ($50.6 \text{ kcal mol}^{-1}$) which is close to the activation energies determined for other semi-ladder polymers [6–8].

Dynamic mechanical behaviour

The temperature at which the principal relaxation, $\tan \delta$, value was a maximum was taken as the dynamic glass transition temperature, T_g . The numerical values obtained from DMA are listed in Table 2. Comparing these values with data from DSC a qualitatively similar dependence on the structure of the polymers under study was found. There are two main causes for the varying differences between the values obtained from DSC and DMA. First, different preparation conditions for the various polymers investigated by DSC meant that the values obtained were not always reproducible. Second, the variable broadness of the glass transition tempera-

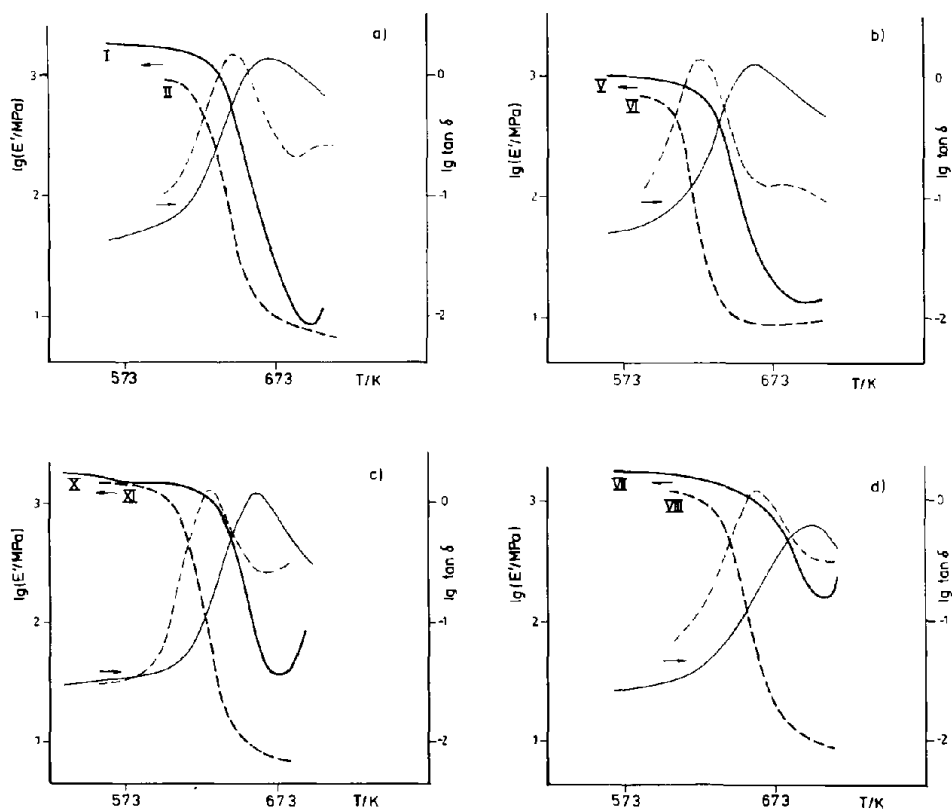


Fig. 5. Dependence of thermal stability on the polymer structure from DMA results.

ture range results in systematic deviations between the corresponding DMA and DSC values.

The DMA results clearly indicate that the introduction of ether linkages into the polymer chain lowers T_g by about 33 K. At the same time however, the thermal stability of the investigated polymer structures is enhanced. The influence of ether linkages on thermal stability is greatest for polymer VII, and is lowest for polymer I. For polymer XIII the temperature-induced changes were so strong that it was impossible to differentiate between polymers XIII and XIV by the measurements carried out. In this case, during the upward heating run (2 K min^{-1}) already conducted below T_g , the

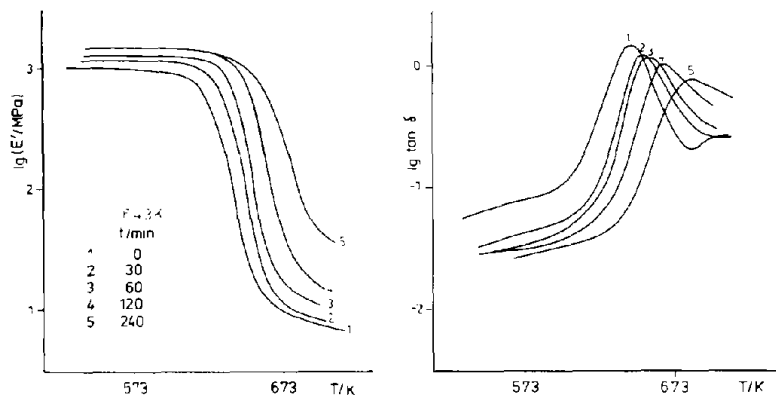


Fig. 6 Change in glass transition temperatures of polymer II at isothermal exposure to 643 K (determined by DMA).

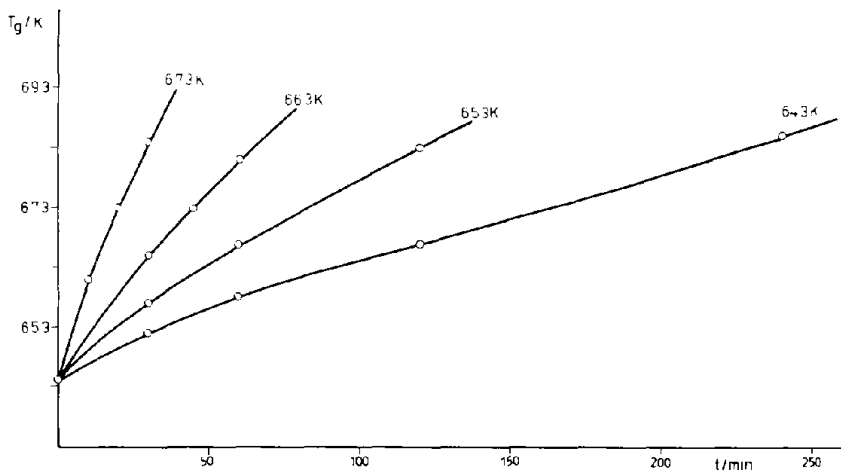


Fig. 7. Change in glass transition temperatures of polymer II, due to isothermal exposure to various temperatures (determined by DMA).

samples changed so greatly that comparable curves could not be obtained. For four polymers, possessing structures with and without ether linkages, the DMA curves are shown in Fig. 5. The higher or lower increases in the modulus at higher temperatures for polymers without ether linkages indicate differences in the intensity of the cross-linking process during the measurements. This is also supported by broadening of the $\tan \delta$ maxima.

The cross-linking process can be determined quantitatively by isothermal temperature exposure of the polymers. DMA curves for samples of polymer II subjected to various exposure times are presented in Fig. 6. The shift of peak temperature, broadening of the $\tan \delta$ maxima, and increase in the "plateau" modulus above T_g can be clearly observed. In order to obtain a quantitative measure for cross-linking the change of T_g with time due to isothermal exposure to various temperatures was plotted (Fig. 7). However, it has to be remembered that these T_g values reflect the simultaneous occurrence of cross-linking and chain scission. According to Augl and Both [9], activation energies can be evaluated from the change in T_g due to isothermal exposure. For the cross-linking process of polymer II an apparent activation energy of 241 kJ mol^{-1} (58 kcal mol^{-1}) was determined.

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