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Differential scanning calorimetric study on the Claisen rearrangement and thermal polymerisation of diallyl ether of bisphenols

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Abstract

The diallyl ethers of bisphenol A (APP), 4,4′-dihydroxy biphenyl (ABP) and bisphenol sulfone (ABS) were synthesised and the kinetics of their thermal rearrangement to the diallyl bisphenols were studied by DSC. The ethers manifested two distinct exotherms corresponding to the Claisen rearrangement of the ether and thermal polymerisation of the rearranged product. The kinetics of both reactions as estimated by the Kissinger and Ozawa methods showed that the rearrangement is disfavoured by the electron-withdrawing substituent and favoured by electron-releasing groups at the *para* position of the allyloxy group. The rate constants calculated from the activation parameters showed the structural dependency. Thus, the rearrangement was facilitated in the order ABP>APP>ABS. The polymerisation kinetics revealed that the polymerisability of the allyl phenols decreased due to the presence of substituent groups on the phenyl ring that can stabilise the free radical formed by way of degenerative transfer at the allylic position. Thus, the polymerisation tendency increased in the order APP>ABP>ABS.

Keywords: Diallyl bisphenols; Claisen rearrangement; Thermal polymerisation; DSC kinetics

1. Introduction

Diallyl bisphenols are important precursors for many thermoset polymer formulations. They are known to react with maleimides, particularly bismaleimides to form tough network polymers with good mechanical properties and thermo mechanical profile [1,15]. In some cases, the phenolic groups are transformed to other reactive groups such as cyanates, serving as network interlinkers in cyanate ester-bismaleimide linked interpenetrating polymers [2]. Commercial polymer formulations such as Matrimide contain diallyl bisphenol A as an important component in blends with bismaleimides [3]. Maleimide reacts with allyl phenols through an Alder-ene reaction also known as Wagner-Jauregg reaction [4,5]. The *o,o′*-diallyl phenols are formed by the thermal, Claisen rearrangement of the corresponding bisallyloxy ethers. The rearrangement is done at carefully controlled temperature conditions to achieve full conversion without risking the polymerisation of the rearranged product. An understanding of the kinetics of the rearrangement would lead to a better control of the conditions for achieving high yield and purity. The Claisen rearrangement of allyl ethers have been studied very early [6,7]. The reaction has been reported to conform to first order kinetics and is generally unca-

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talysed. Substituent effect on the reaction rate has also been investigated [8,9]. Generally, such kinetics are followed by the estimation of the formed phenol by suitable methods. We observed that the rearrangement reaction proceeds exothermically and if the reaction temperature is not controlled, concomitant polymerisation could also proceed. Knowledge of the kinetics of rearrangement and polymerisation would be useful in selecting conditions for getting optimum yield of the rearranged product. In this perspective, the kinetics of thermal rearrangement and polymerisation were followed. Since DSC showed clear exotherms characteristic of both the reactions, this method appeared an easier tool for monitoring the reaction kinetics. The kinetics of Claisen rearrangement of bisallyloxy ethers has not been reported. We have recently studied the Claisen rearrangement of bispropargyl ether resins using DSC [10] and established the structure-thermal property correlation. In the present paper, we report the kinetics of Claisen rearrangement of three different diallyl ethers by DSC and examine the structural dependency. The kinetics of the thermal polymerisation of the rearranged product is also described.

2. Experimental part

2.1. Materials

Bisphenol A (BPA, SD Fine Chemicals, India), 4,4$'$-dihydroxy biphenyl (DHB, E-Merck, Germany), bis (4-hydroxyphenyl) sulphone (BPS, E-Merck, Germany) were used as received. Allyl bromide (Spectrochem, India) was purified by distillation. Analytical grade acetone and potassium carbonate (CDH, India) were used as received. Other solvents were of laboratory grade.

2.2. Instruments

2.2.1. DSC analysis

DSC experiments were performed at varying heating rates in static air using a MettlerTA 3000 Thermal Analyser system in conjunction with a TC-10ATA processor and a standard DSC-20 apparatus. About 5 mg of the dry sample was weighed and encapsulated in 40 ml Al cups with a pinhole and was used for DSC analysis. The temperature and heat flow calibrations were done by the recommended procedure using pure indium metal of melting point 156.6°C and heat of fusion, $DH_f=28.45$ J/g. The enthalpy of curing, DH was determined from the area under the exothermic peak and the sample mass.

Conversion at any temperature, a_T was found from the relation, $a_T=DH_f/DH_T$, where DH_f is the fractional enthalpy at that temperature and DH_T the total heat of reaction, obtained by the fractional and total areas, respectively, under the exothermic curve.

NMR analysis was performed using a Brucker model 300 MHz FTNMR spectrometer.

2.3. Syntheses of 2,2-bis (4-allyloxy phenyl) propane (APP), 4,4$'$-allyloxy biphenyl (ABP) and bis (4-allyloxy phenyl) sulphone (ABS)

APP was synthesised by reacting BPA (22.8 g, 0.1 mol) with allyl bromide (26.6 g, 0.22 mol) in presence of potassium carbonate (42 g, 0.30 mol) in refluxing acetone for 20 h. The solution was filtered and the filtrate was evaporated. The residue was dissolved in dichloromethane and washed with dilute sodium carbonate solution several times followed by water till free from alkali. After drying over anhydrous sodium sulphate, the solvent was distilled off and the product was dried in vacuum at 50°C/8 h to get a colourless oil in 95% yield. It was characterised by OH-value (nil) and proton NMR both confirming the structure.

ABP and APS were synthesised similarly. In these cases, the white solid obtained was recrystallised from methanol to get white shining crystals in almost quantitative yields. They were characterised by NMR.

2.3.1. NMR

APP ($CDCl_3$), δ (ppm): 1.25 (s, 6H, isopropyl), 4.6 (d, 2H, O–CH_2–), 5.25 (m, 2H, =CH_2), 6.1 (m,1H, =CH–), 6.8–7.0 (m, 4H, aromatic$'$)

ABP (d_6 acetone), δ (ppm): 4.6 (d, 2H, O–CH_2–), 5.2–5.5 (m, 2H, =CH_2), 6.1 (m,1H, =CH–), 7.0 (d, 2H, aromatic,2,2$'$), 7.5 (d, 2H aromatic, 3,3)

ABS (d_6 acetone), δ (ppm): 4.6 (d, 2H, O–CH_2–), 5.3 (m, 2H, =CH_2), 6 (m,1H, =CH–), 6.9 (d, 2H, aromatic, 2,2$'$), 7.8 (d, 2H aromatic, 3,3$'$)

2.4. Thermal rearrangement

The diallyl ether, APP was heated at 180°C for 28 h in an air oven. The progress of the reaction was followed by estimating the OH value of the product. The final product was characterised by OH value and by NMR.

OH value 364 mg KOH/g (theor.: 366 mg KOH/g)

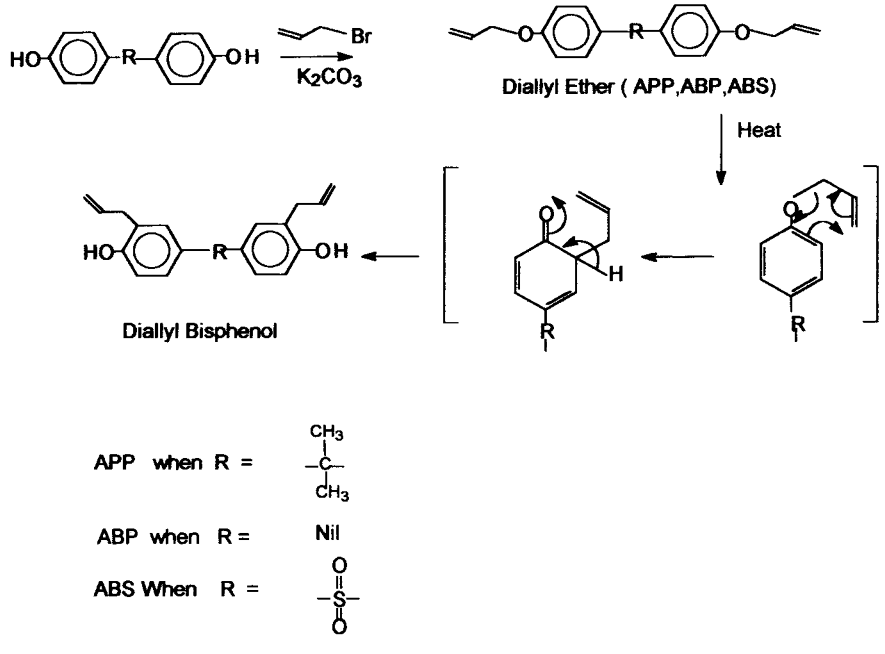
NMR ($CDCl_3$), δ (ppm): 1.25 (s, 6H, isopropyl), 3.1 (d, 2H, Ph–CH_2–), 5.1 (m, 2H, =CH_2), 6.0 (m, 1H, =CH–), 6.8–7.0 (m, 4H, aromatic)

3. Results and discussion

3.1. DSC analyses

The diallyl ethers of the three bisphenols viz; bisphenol A, bisphenol sulphone and 4,4′-dihydroxy biphenyl were synthesised as per Scheme 1 and were characterised by OH value and proton NMR, both conforming to expected structure. Allyl phenyl ethers, on heating are known to undergo exothermic sigmatropic rearrangement to the *o*-allyl phenols. The diallyl phenols required for commercial resin formulations are made this way. Unless carefully controlled, the rearrangement performed at higher temperature could be accompanied by undesired polymerisation of the allyl functions. The dynamic DSC of the three compounds are shown in Fig. 1. All thermograms showed two exotherms and the results of the DSC peak maxima of the two exotherms of the monomers, obtained at five heating rates are given in Table 1. The peak temperatures increase systematically with increase in heating rates.

The first exotherm corresponded to the rearrangement and the second, to the curing of the rearranged product. This was confirmed from the DSC analysis of the pure rearranged product in the case of APP (also shown in Fig. 1) which showed a single exotherm at the temperature range corresponding to the second exotherm in the DSC of the allyl ether. In the cases of APP and ABP, the two exotherms were well separated whereas for ABS, a partial overlap was seen, although the exotherm maxima were distinguished. The rearrangement occurred at more or less same temperature for the first two cases, whereas ABS underwent rearrangement at a relatively higher temperature. In addition to the melting transition at 140°C, another endotherm corresponding to liquid crystalline transition was observed at 160°C for ABP. The liquid crystalline transition was confirmed by the visual



Scheme 1.

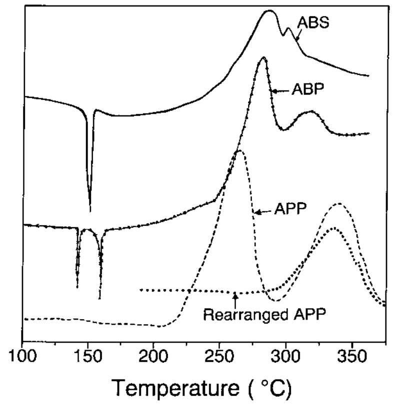


Fig. 1. DSC thermograms of the diallyl ethers and the rearranged product of APP. Heating rate 10°C/min.

observation of heated ABP under a polarised optical microscope[1].

3.2. Kinetic analysis

It was of interest to study the kinetics of both the rearrangement and polymerisation reaction from the DSC. Since the peaks corresponding to these two reactions are not well resolved, permitting area integration except in the case of APP, the non-isothermal methods were not employed for the kinetic analyses. Instead, the two well known variable heating rate methods, which depend on peak maxima in DSC were employed for the purpose where, the apparent variations in activation parameters caused by heating rates are taken care of. Moreover, these methods do not invoke reaction order n or fractional conversion α in deriving the kinetic parameters. The Kissinger's and Ozawa's methods, based on variable heating rate were used for finding the activation parameters and their dependency on structure of the compounds.

Kissinger's method makes use of the Eq. (1) [11]

$$\frac{2.303\,\mathrm{d}[\log(\phi/T_\mathrm{m}^2)]}{\mathrm{d}(1/T_\mathrm{m})} = \frac{-E}{R} \tag{1}$$

where T_m is the temperature corresponding to the maximum in the DSC exotherm at a heating rate, ϕ.

Table 1
DSC peak maxima (in °C) for various systems[a]

Heating rate (°C/min)	ABS		APP		ABP	
	T_{m1}	T_{m2}	T_{m1}	T_{m2}	T_{m1}	T_{m2}
2	240	255	235	300	240	–
5	262	275	253	320	255	293
7	270	282	260	347	259	300
10	280	293	268	342	269	310
15	291	303	274	370	275	328

[a] 1: Rearrangement; 2: polymerisation.

The slope of the linear plot of $\log(\phi/T_\mathrm{m}^2)$against $1/T_\mathrm{m}$ gives E. Ozawa's method uses a similar equation as [12,16,17]

$$\frac{2.15\,\mathrm{d}[\log(\phi)]}{\mathrm{d}(1/T_\mathrm{m})} = \frac{-E}{R} \tag{2}$$

E, obtained from the slope of the plot of log ϕ against $1/T_\mathrm{m}$, is refined by iteration, making use of a two-term approximation for the Arrhenius temperature [13]

$$p(x) = \mathrm{e}^{-x}\left[\frac{x+1}{x+3}\right] \quad \text{where } x = \frac{E}{RT} \tag{3}$$

The theoretical slope (D) of the above equation is $-1-2/x+1/(1+x)-1/(x+3)$. The process of iteration was continued to get a constant value for $E=2.303R\times\text{Slope (exp)}/D$. This refinement is recommended for Ozawa method in ASTM E 698 [14].

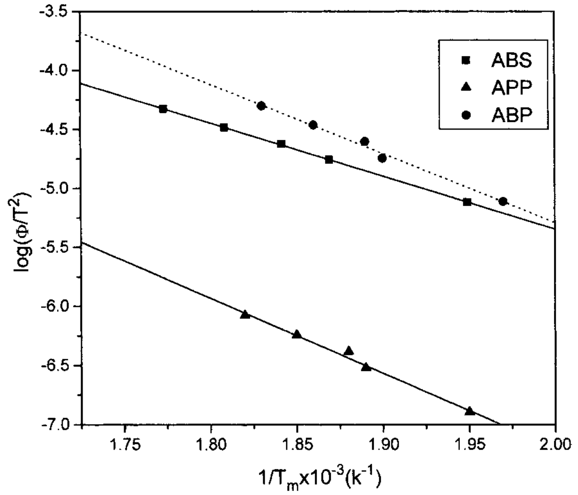


Fig. 2. Determination of activation parameters by Kissinger's method for rearrangement reaction of the three monomers.

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[1] The authors thank Mrs. J.D. Sudha, Regional Research Laboratory, Trivandrum, for performing this experiment and confirming the observation.

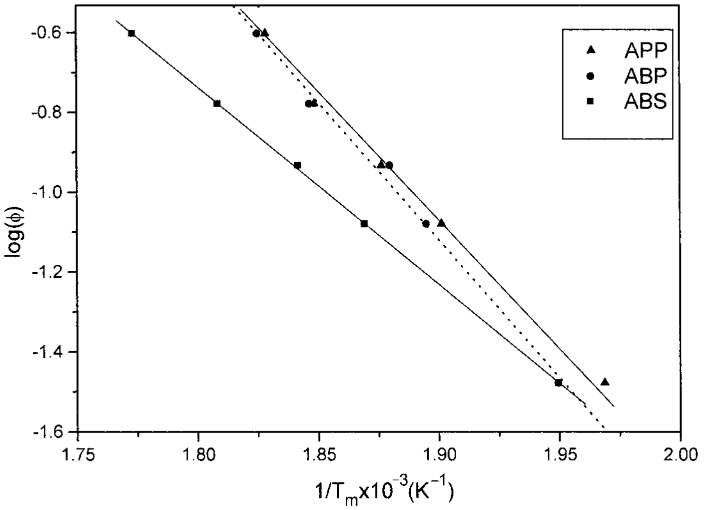


Fig. 3. Determination of activation parameters by Ozawa's method for rearrangement reaction of the three monomers.

Typical kinetic plots by Kissinger's and Ozawa's methods are shown in Figs. 2 and 3, respectively.

A was found in both cases from the relation

$$A = \frac{\phi E\, e^{E/RT_m}}{RT_m^2} \tag{4}$$

The activation parameters are given in Table 2 for all the three compounds for both the rearrangement and cure reactions. Both the methods give nearly identical values for a given reaction.

3.3. Kinetics of rearrangement reaction

The activation energy for rearrangement reaction is lowest for the sulphone compound. Although structural dependency on activation parameters has not been disclosed, Claisen rearrangement has been reported to be retarded by electron-withdrawing groups on the phenyl ring. Thus, replacement of amino group by nitro group in phenyl allyl ethers retarded the reaction 20-fold [8,9]. The lowest E value for ABS implies a kinetically facile rearrangement reaction, which is not in league with the electronic effect of the sulphone substituents. Moreover, the thermogram shows a higher temperature regime for the rearrangement of ABS. Since rate constant depends on both A and E by the Arrhenius relationship, $k=Ae^{-E/RT}$, the value of E alone does not give a correct idea about the facile nature of the reaction. Therefore, the rate constants were computed using the E and A values for various temperatures and plotted in Fig. 4. This shows that the rate of reaction decreases in the order

$$\mathrm{ABP} > \mathrm{APP} > \mathrm{ABS}$$

Claisen rearrangement can be facilitated by the electron density on the phenyl ring. In ABP, the presence

Table 2
Kinetic parameters determined by Kissinger and Ozawa methods

Monomer	Kissinger				Ozawa			
	Rearrangement		Polymerisation		Rearrangement		Polymerisation	
	E (kJ/mol)	A (s^{-1})	E (kJ/mol)	A (s^{-1})	E (kJ/mol)	A (s^{-1})	E (kJ/mol)	A (s^{-1})
APP	107.9	1.23×10^8	74.1	3.17×10^4	107.4	1.48×10^8	74.7	3.24×10^4
ABS	86.1	1.31×10^6	97.2	4.96×10^5	87.0	1.63×10^6	97.7	5.10×10^5
ABP	123.5	8.30×10^9	77.3	3.78×10^4	123.8	9.43×10^9	78.4	4.15×10^4

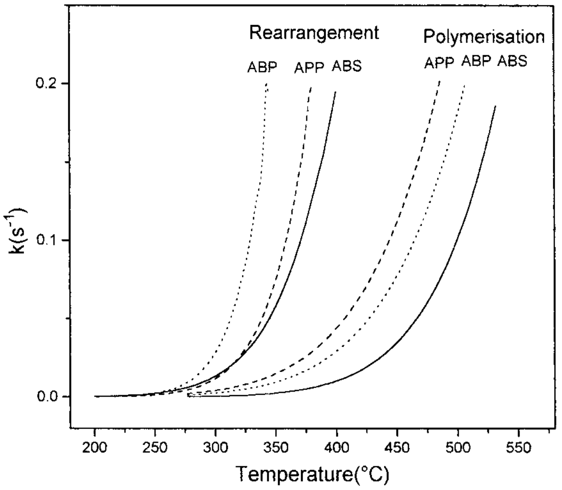


Fig. 4. Temperature dependency of rate constants for rearrangement and polymerisation for the three monomers.

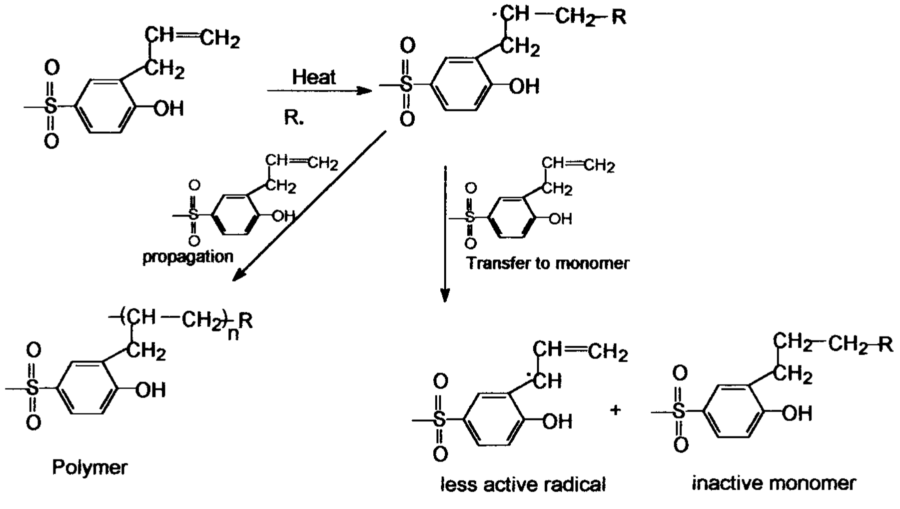
of another allyloxy phenyl group at the *para* position is conducive for rendering the phenyl ring relatively more electron-rich (through $+R$ effect) than in the case of APP having only an isopropyl group which can, at best, contribute to electron density of the phenyl ring through $+I$ effect only. The electron-withdrawing sulphone group in ABS retards the reaction. The observed reactivity order is in keeping with the electronic effect of the substituent at the *para* position of the allyloxy group. The mechanism of rearrangement is included in Scheme 1.

3.4. Kinetics of thermal polymerisation

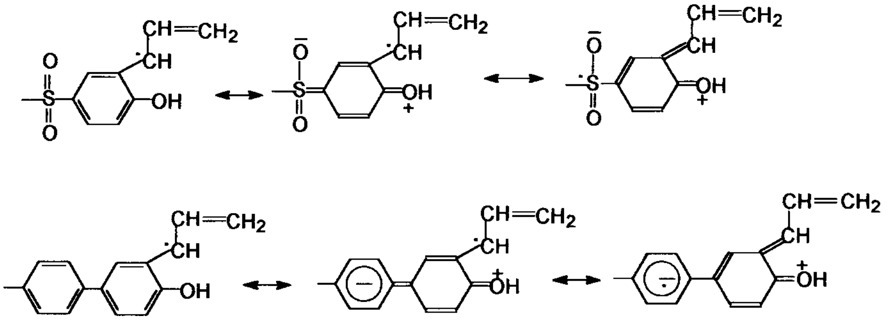
DSC indicated thermal polymerisation following the rearrangement. The kinetic constants were calculated for the polymerisation reaction by the Kissinger and Ozawa methods. The A and E values are compiled in Table 2. As done in the case of rearrangement reaction, the rate constants at different temperatures were calculated from A and E (included in Fig. 4) from which, it is found that the polymerisability increases in the order:

APP > ABP > ABS

Under pure thermal conditions, the allylic groups polymerise by free radical process. Allylic double bonds are sluggish in radical polymerisation for two reasons. The double bonds are not activated. Secondly, the degenerative radical transfer at the allylic position giving rise to a stable radical retards the polymerisation. In the present cases, the activity of the double bonds cannot vary significantly among the three monomers. Hence, the difference in polymerisability must be arising from the difference in efficiency of degenerative chain transfer at the allylic (also benzylic) position. The polymerisation mechanism and the transfer reaction are shown in Scheme 2. It can be seen that the allylic radical can be more stabilised through extended delocalisation with the various mesomeric forms of the *para* sulphonyl- (derived from ABS) and *para* phenyl (derived from ABP) substituted *o*-allyl phenols as shown in Scheme 3. For the former, the



Scheme 2.



Scheme 3.

radical located on the sulphur atom can be expected to be quite stable. However, in case of APP, this delocalisation is limited to the adjacent phenyl group only. It can, therefore, be expected that the stability of the allylic (also benzylic) radical after the transfer increases in the order ABS>ABP>APP, facilitating the degenerative transfer in the same order. As a consequence of this, the polymerisability of the monomers is expected to be in the reverse order, viz. APP>ABP>ABS and the kinetic study confirms this.

4. Conclusions

The diallyl ethers of the bisphenols manifested two distinct exotherms corresponding to the Claisen rearrangement and thermal polymerisation. The kinetics of both reactions as studied by dynamic DSC showed that the rearrangement is disfavoured by the electron-withdrawing substituent and favoured by electron-releasing groups at the *para* position of the allyloxy phenyl group. The rate constants calculated from the activation parameters evidenced it. The polymerisation kinetics revealed that the polymerisability decreases by the presence of substituent groups on the phenyl ring that can stabilise the free radical formed by way of degenerative transfer at the allylic position.

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