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Di-styrene-ethers.
A novel class of cationically polymerizable oligomers

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Summary

A novel class of cationically polymerizable oligomers is reported. The system is based on di-styrene-ethers, a series of which were synthesized and characterized. The synthesized compounds were thermally polymerized by a cationic mechanism. Bisphenol-A diethoxy vinyl ether, which is known readily to undergo cationic polymerization was used as a reference compound. By comparison it was shown that this new class of oligomer reacts much more rapidly in thermally initiated cationic polymerization.

Introduction

For many years, cationic polymerization was something that was carried out at low temperatures using initiators that were difficult to handle under normal conditions. To a large extent this was changed by the development of iodonium- and sulfonium-salts (1,2,3) containing non-nucleofilic counterions. In these systems the initiating Brönstedt acid is produced by exposing the initiator to UV-light. This makes it possible to mix the monomer and the latent initiator and store them under ambient conditions. It has also been shown that both iodonium- (4) and sulfonium-salts (5) can be thermally activated. These developments have made it possible to use cationic polymerization in coating applications and for thermosets. While a lot of research have been focused on developing new onium salts and to interpreting their decomposition mechanism, very little has been done on the synthesis of new oligomers for cationic curing.

The oligomers most widely used today for cationic cured coatings are cyclo aliphatic epoxides. These compounds readily undergo cationic polymerization but they are rather slow systems since the activation energy for the ring opening step is relatively high. An alternative to the epoxides has been oligomers based on vinyl ethers (6), which are known rapidly to undergo cationic polymerization (7). So far, very few oligomers based on vinyl ethers have been commercially available. The goal of this work has been to develop an alternative to vinyl ethers.

Higashimura and coworkers (8) has shown that styrene-ethers, like p-vinylanisole, are as reactive as vinyl ethers in cationic polymerization. Based on this we have developed a new class of cationically polymerizable oligomers, di-styrene-ethers (figure 1).

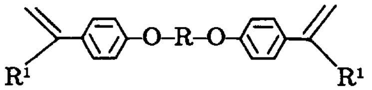

figure 1

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Experimental

General. 4-hydroxybenzaldehyde, potassium hexafluorophosphate, 1,4-dibromo -2-butane, α,α'-dibromo-*p*-xylene, α,α'-dibromo-*m*-xylene, α,α'-dibromo-*o*-xylene, were purchased from Merck. *p*-hydroxyacetophenone, 1,3-dibromopropane, 1,4-dibromobutane , 1,10-dibromodecane and methyltriphenylphosphonium bromide from Aldrich. Diphenyliodonium chloride from Fluka AB. Copper(II)benzoate from Labkemi AB. All the chemicals were used without further purification. The solvent, THF, was purified by distillation.

Analysis. The reactions were followed by thin layer liquid chromatography (TLC) with eluent hexane:ethylacetate, 1:1. The plates used were silica gel 60 F_{254} (Merck). The synthesized di-styrene-ethers (I-VIII) were characterized by IR, NMR and elemental analysis. The instruments were, in order, Perkin-Elmer FTIR 1710 and Bruker NMR WP 200. The elemental analysis was conducted by Micro-Kemi AB in Uppsala, Sweden. Melting points were determined on a Perkin-Elmer DSC 2. The thermally initiated polymerizations were conducted on the same DSC.

General synthesis of di-styrene-ethers (I-VIII). All equipment was dried and held under nitrogen during the synthesis procedure. The reaction mixtures were continuously stirred by a magnetic stirrer.Methyltriphenylphosphonium bromide (21,4 g; 60 mmol) and a catalytic amount of 18-crown-6 were dispersed in 100 ml dry THF. Potassium tert-butoxide (13.4 g; 120 mmol) was added to this white slurry. The mixture was kept on ice. The yellow suspension which formed was allowed to react for 30 minutes. For compound I-VII *p*-hydroxybenzaldehyde (7.4 g; 60 mmol) dissolved in 50 ml THF, was then added. For compound VIII, *p*-hydroxyacetophenone (8.2 g; 60 mmol) was added. The reactions were complete after one hour shown by TLC. The corresponding dibromide (30 mmol) and an additional amount of potassium tert-butoxide (3.4 g; 30 mmol) were now added. The ice was removed and the reaction mixture was allowed to stand for about sixteen hours (overnight).

Work-up: The potassium bromide was first removed by centrifugation followed by evaporation of most of the solvent. The residue was dissolved in warm ethanol and the product precipitated in refrigerator. The products were recrystallized from ethyl acetate/hexane to give yields between 25 and 66 % (table 1). Melting points and elemental analysis (table 1). FTIR (1177; 1244; 1627; 2955; 3090 cm^{-1}). ^{1}H-NMR ($CDCl_3$) (figure 2). ^{13}C-NMR ($CDCl_3$) (figure 3).

Synthesis of diaryliodonium salt. Diphenyliodonium chloride (3.7 g; 12 mmol) and potassium hexafluorophosphate (2.2 g; 12 mmol) were dissolved and mixed in water at room temperature. The white solid formed was filtered off and dried to give 2.7 g diphenyliodonium hexafluorophosphate (55 %). Melting point 168-170 °C. The product was confirmed by IR.

Thermally initiated cationic polymerization of di-styrene-ethers (I-VIII). Di-styrene-ether (I-VIII; 5 mg), diphenyliodonium salt (0,25 mg) and copper(II)benzoate (0,025 mg) were placed in the DSC-sample cup. The same procedure was carried out for the reference compound bisphenol-A diethoxy vinyl ether (BPA-DEVE). The samples were heated from 320 to 450 K at a rate of 10 K/min. The initiator in this particular system was activated at 360 K. For the lower melting monomers the polymerizations started at this point and for the higher melting ones at their respective melting points. The endothermic melting peaks and the exothermic polymerization peaks were recorded (figure 4).

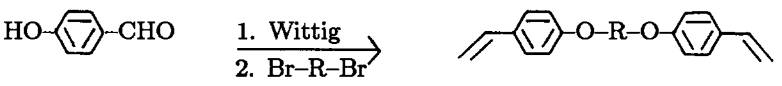
	R	MW	mp °C	yield %	% C	% H	% O
I.	$-(-CH_2-)_3-$	280	128	38	80.5	7.1	12.4
					(81.4)	(7.1)	(11.5)
II.	$-(-CH_2-)_4-$	294	130	48	81.7	7.7	10.6
					(81.6)	(7.5)	(10.9)
III.	$-(-CH_2-)_{10}-$	378	111	34	82.8	9.3	7.9
					(82.5)	(9.0)	(8.5)
IV.	$-(-CH_2CHCHCH_2-)-$	292	127	66	82.1	7.0	10.9
					(82.2)	(6.8)	(11.0)
V.	$-(-CH_2-(-p\text{-Ph}-)-CH_2-)-$	342	–	25	83.5	6.5	10.0
					(84.2)	(6.4)	(9.4)
VI.	$-(-CH_2-(-m\text{-Ph}-)-CH_2-)-$	342	95	60	84.2	6.6	9.2
					(84.2)	(6.4)	(9.4)
VII.	$-(-CH_2-(-o\text{-Ph}-)-CH_2-)-$	342	64	34	83.1	6.5	10.4
					(84.2)	(6.4)	(9.4)
VIII.	$-(-CH_2CHCHCH_2-)-$	320	151	33	82.5	7.9	9.6
					(82.5)	(7.5)	(10.0)

Table 1. Characteristics and elemental analysis data of the synthesized di-styrene-ethers (figure 1)(for I–VII, R^1=H; for VIII $R^1=CH_3$). Elemental analysis shows found and (calculated) values.

V has no melting point but decomposes at about 300 °C.

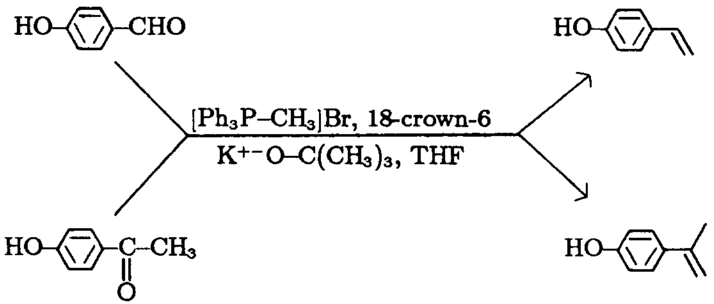
Results and discussion

Synthesis and characterization of di-styrene-ethers. When this class of compounds is to be synthesized there are two functional entities to consider, namely an ether and a vinyl group. A lot of classical reactions are known for this purpose, depending on the starting materials. As mentioned earlier, our goal was to synthesize styrene derivatives having an ether in paraposition, and we decided that p-benzaldehyde should be a convenient starting molecule. From this it is easy to obtain the vinyl group by using Wittig conditions. Moreover, the phenolic alcohol is a good nucleophile for the ether formation. This second step is carried out by treatment with a base and the corresponding dibromide (scheme 1).

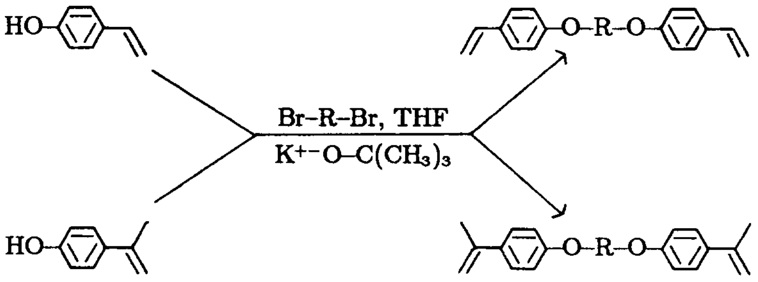


scheme 1

The reaction conditions in the ether step are SN2, and this has to be considered when choosing the dibromides. It is known that benzylic and allylic groups gives good yields and high rates in ether synthesis. Primary aliphatic groups are satisfactory, secondary are not very good and tertiary are very poor. Considering these facts the dibromides were chosen as shown in table 1. This gives eight compounds (I–VIII) with different characteristics as far as polymerisation rates, melting points and mechanical properties are concerned. After the initial experiments, it was found that the best experimental conditions were obtained if the Wittig reaction is carried out before the ether step, because the aldehyde is sensitive to the basic conditions and would give undesirable side reactions. The reaction conditions used also work for ketones, and one α-methylstyrene derivative was also synthesized, in this case with *p*-hydroxyacetophenone as starting material. This should make it possible to compare the polymerization rates of styrene and α-methylstyrene derivatives. The overall reaction conditions for the di-styrene-ethers are shown in schemes 2 and 3.



Scheme 2



Scheme 3

According to TLC, the yield for the Wittig reaction is 100 %. The overall yields and the properties of the synthesized compounds (I–VIII) are shown in table 1. It should be noted that no attempts have been made to improve the yields.

The di-styrene-ethers were characterised by NMR (^{13}C, ^{1}H; figures 2 and 3 shows two characteristic examples), IR (experimental section) and by elemental analysis (table 1). Melting points were determined by DSC (table 1).

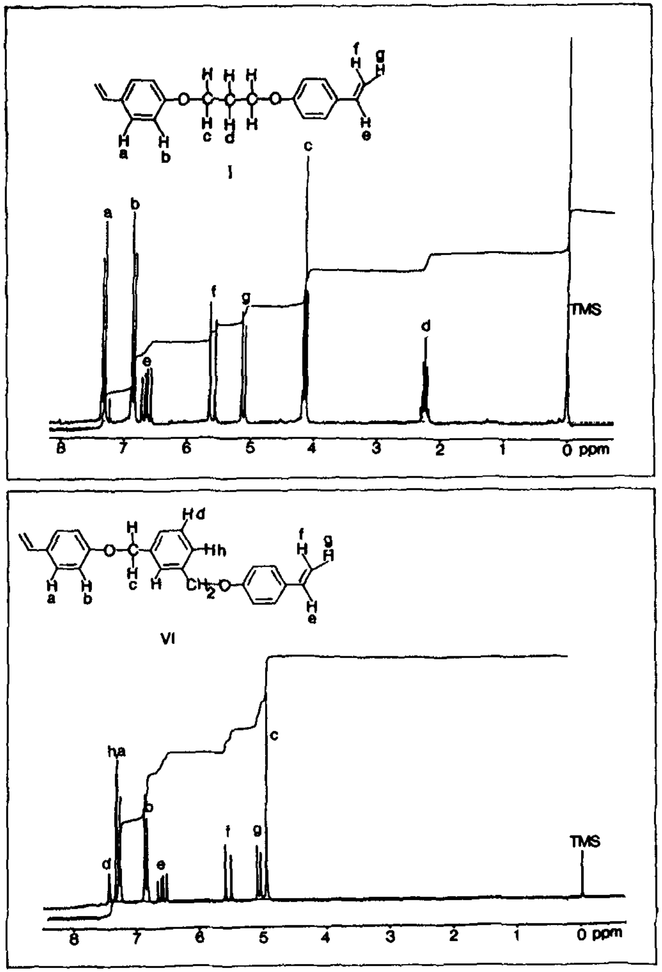


Figure 2. ^{1}H shifts of two typical di-styrene-ethers.

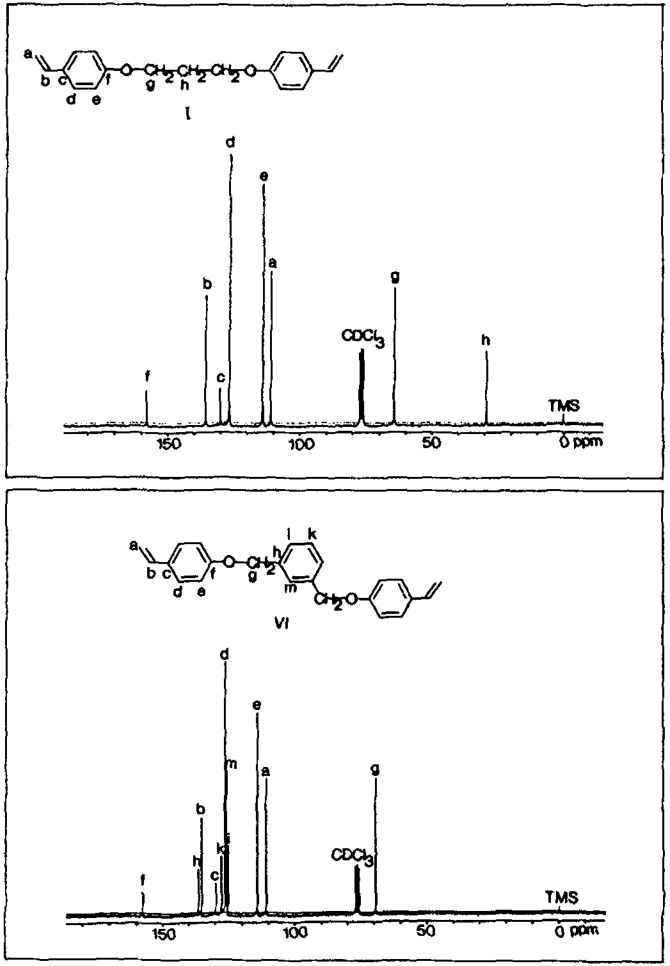


Figure 3. ^{13}C shifts of two typical di-styrene-ethers.

Polymerization of di-styrene-ethers. The synthesized compounds are readily polymerized in the presence of a cationic initiator which is thermally activated. The activating temperature is specific, and depends on the composition of the initiating system. A general mechanism for the initiation and polymerization is shown in scheme 4 (9).

$$\text{Red-H} + \text{Cu(II)L}_2 \longrightarrow \text{Red} + \text{Cu(I)L} + \text{HL}$$

$$\text{Ar}_2\text{I}^+\text{X}^- + \text{Cu(I)L} \longrightarrow \text{ArI} + [\text{ArCu(III)LX}]$$

$$[\text{ArCu(III)LX}] + \text{M} \longrightarrow \text{Ar–M}^+\text{X}^- + \text{Cu(I)L}$$

$$\text{Ar–M}^+\text{X}^- + n\text{M} \longrightarrow \text{Ar–(–M–)–M}^+\text{X}^-$$

scheme 4

Several initiators are available and can be chosen depending on the desired curing temperature. In this work a diphenyliodonium hexafluorophosphate /copper(II)benzoate initiating system which becomes active at 80 °C was used. Cationic polymerization of this new class of monomers is expected to proceed at a high rate, since *p*-methoxystyrene is known (10) to be a very fast reacting monomer in cationic polymerization, actually of the order of three magnitudes faster than styrene itself. Since the structure of this new class of monomers is similar to *p*-methoxystyrene, the kinetics is expected to be about the same. The most important reason for the high polymerization rate of this type of structure is that an ether in the para position can stabilize the propagating chain by resonance. DSC-curves of the melting endotherms and the polymerization exotherms were recorded (figure 4), for di-styrene-ethers (I-VIII) and a reference compound, namely bisphenol-A diethoxy vinylether (BPA-DEVE), which is known very rapidly to undergo cationic polymerization. This shows that this novel class of oligomer is very rapidly polymerized by a cationic mechanism, and at a considerably higher rate than the reference vinyl ether. Figure 4 also shows that VIII is a faster reacting oligomer than II. This depends on the higher stability of the propagating chain in the di-(α-methylstyrene)-ether. It can also be seen that VI is slower than the other two, which is probably an effect of the more fixed conformation for this benzylic type of oligomer which gives the propagating chain less freedom to move.

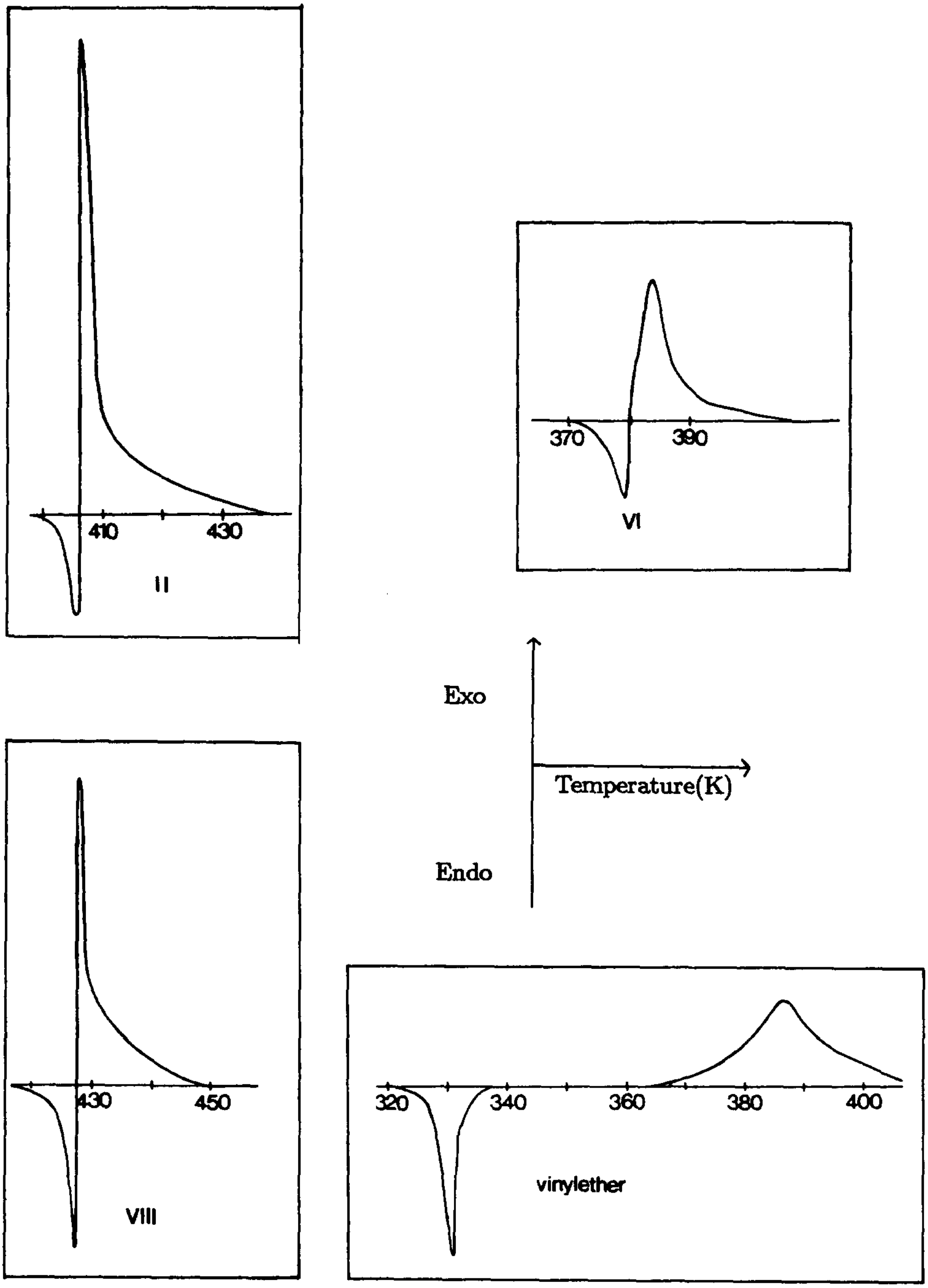


Figure 4. Recorded DSC-spectra showing the endothermic melting and exothermic polymerization of three typical di-styrene-ethers and the reference vinyl ether (BPA-DEVE).

Acknowledgements

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