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The synthesis and characterization of novel thermosettable vinylbenzyl terminated monomers and the properties of the cured resins

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Summary

A new process for the synthesis of thermally reactive VBT monomers(I-VIII) has been developed. The vinylbenzyl etherification of aromatic hydroxyl groups with >99% conversion in polar aprotic solvents has been achieved. The conversion of the aromatic hydroxyl groups has influence on the physical properties, especially on dielectric property of the cured resins. A series of novel VBT monomers were prepared by this process and their cured products all show exceptional thermal stability, good dielectric properties and moisture resistance. The VBT monomers appear to be very attractive candidates for use in electrical and electronic applications.

Introduction

Vinylbenzyl ethers of polyphenols are a new class of thermosetting resins. They can be cured thermally with no evolution of volatiles. The cured resins have high glass transition temperature, good thermal stability, excellent moisture resistance and low dielectric constant[1]. Therefore, the vinylbenzyl terminated [VBT] monomers appear to be very attractive candidates for use in electrical and electronic applications. This paper reveals the preparation and structural characterization of a series of novel VBT monomers. The electrical and thermal properties of the cured resins will also be briefly discussed.

Results and discussion

Synthesis and structural characterization

Novel VBT monomers(I-VIII) were synthesized in two steps via insitu formed phenoxides followed by coupling with vinylbenzyl chloride(VBC) under basic conditions(Scheme 1). The backbones of I-VIII selected here for examination are listed. They can be divided into two general groups. Structures I-IV consist of aliphatic or cycloaliphatic units in the backbone with ortho-methyl substituents on the aromatic rings. We expect that this type of structure will provide the cured resins with hydrophobic properties. Structures V-VII all contain meta-bromine substituents on the aromatic moieties with ortho-methyl groups. Within this group the aromatic skeletons varied from biphenyl to bisphenol-F. The backbone of structure VIII, unlike the preceding examples, is tetrabromobisphenol-A which

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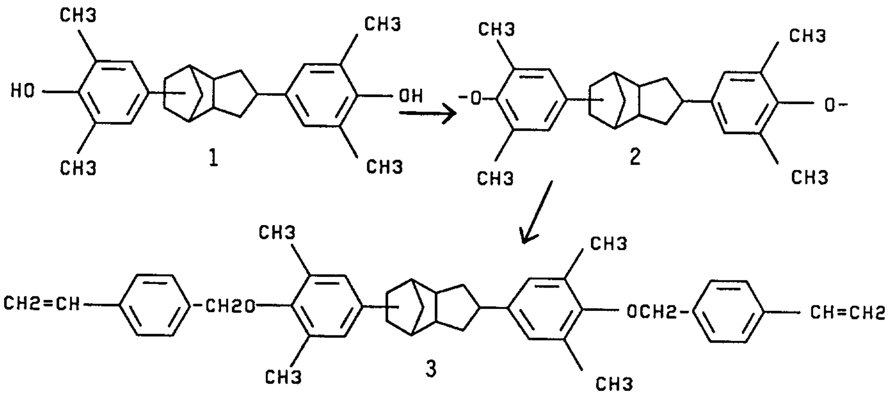
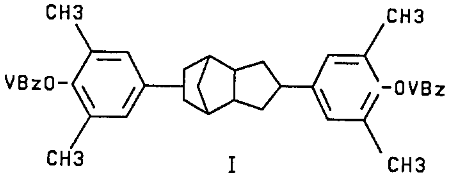


Scheme 1 Synthetic pathway for VBT monomer 1



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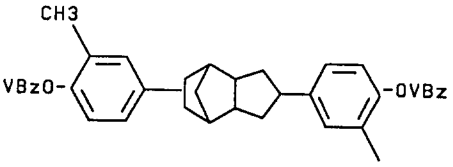

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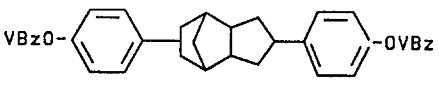

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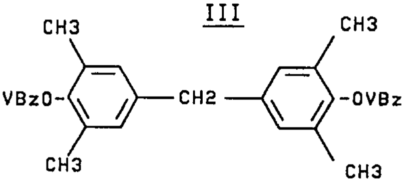

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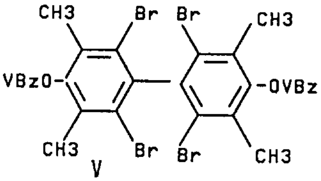
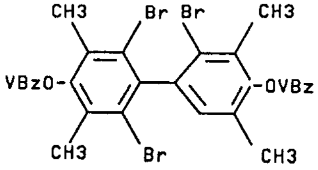
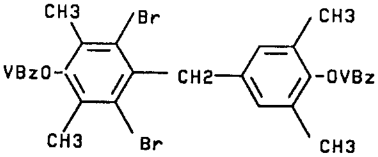


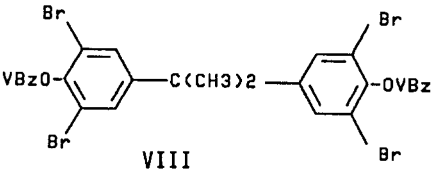
V



VI



VII



VIII

doesn't have methyl substituents. A few VBT monomers have been prepared previously by using polar solvents such as methyl alcohol in the presence of an alkali metal[2-3]. The monomers prepared by this method contain a portion of unreacted phenolic hydroxyl groups. In our process, two types of solvents were selected for comparison - polar aprotic solvents, such as dimethylformamide(DMF), dimethylsulfoxide(DMSO), and n-methylpyrrolidinone (NMP) and protic solvents, such as methanol, n-propanol, or methanol-acetone mixture. It was found that at the same ratio of phenolic hydroxyl group to vinylbenzyl chloride (1.25eq.VBC/ leq.ArOH), high conversion(>99%) of the phenoxides into vinylbenzyl ethers was achieved at low temperature by using a polar aprotic solvent as shown in Table 1. In most cases, the etherification reaction of polyphenols only reach <94% or less conversion of aromatic phenolic hydroxyl groups when polar solvents were used. In the polar aprotic solvents such as DMF, the phenoxide ions were freed from entanglement with the solvent and the counter cations (Na^+), thus becoming a very strong nucleophile and leading to a high conversion of phenolic OH. The reaction is very fast and the reaction course can be followed by the disappearance of the dark green color of the phenoxide ions[4-6].

Table 1. **Solvent effect on the conversion of phenolic hydroxyl group**

Monomers	**Solvent**	**Conversion**
I	DMF	>99%
I	DMAC	>99%
I	Acetone-Methanol	<94%
II	DMF	>99%
II	Acetone-Methanol	<93%

The structures of I-VIII were confirmed by infrared spectra as well as by ^1H NMR analysis to be bisvinylbenzyl ethers of the corresponding polyphenols.The characteristic absorption bands for the vinylbenzyl group appeared in the area of $900cm^{-1}$ and $990cm^{-1}$. The broad phenolic OH band for polyphenols at $3200\text{-}3600cm^{-1}$ disappeared indicating the high phenolic OH conversion when polar aprotic solvents were used(**Figure 1**). The structures of benzyl ethers of polyphenols were readily ascertained from the analyses of the ^1H NMR spectra of the products. A singlet resonance signal for the protons of the benzyl methylene group appeared at the 4.7-4.8ppm area which relates to the regioselective formation of vinylbenzyl ethers. A clear proton splitting pattern in the 5-7ppm area for vinyl olefinic protons was observed by ^1H NMR(**Figure 2**). Protons a, b, and c are magnetically non-equivalent, and show spin-spin coupling with $J_{ab}>J_{ac}>J_{bc}$. This is typical for olefinic protons with more interaction between protons which are trans to each other than for protons which are cis to each other.

Reactivity of VBT monomers

VBT monomers and oligomers can be cured thermally or through a radical initiated addition reaction. The curing process features no evolution of volatiles. There are a few known reactive groups such as cyanate[7-9], maleicimide-ene[10-14], acetylene[15-17], benzocyclobutene[18-21],etc., which undergo thermal polymerization via ring formation or stepwise addition crosslinking. However, the thermal crosslinking mechanism for VBT polyphenols is expected to be much simpler than that of the above mentioned reactive groups. Reactivities of VBT polyphenols I-VIII were measured by means of a differential scanning caloriric method(DSC) and are listed in **Table 2**. Both nonbrominated monomers(I-II, IV) and brominated

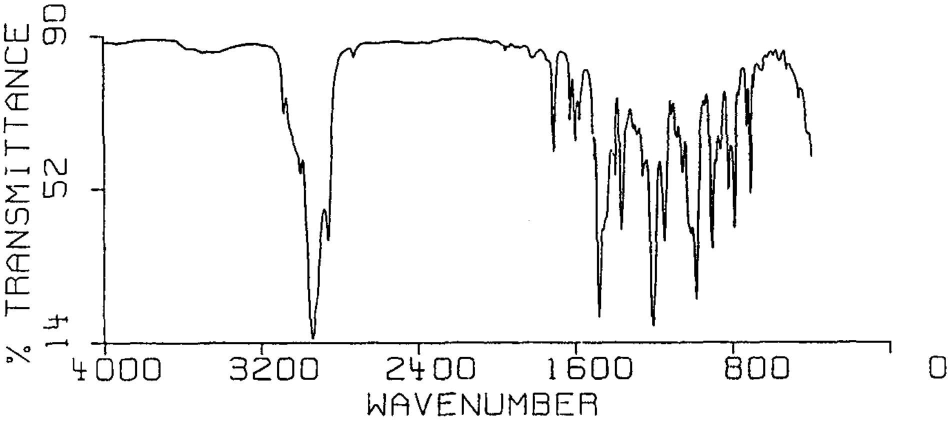


Figure 1 IR for VBT monomer I, neat

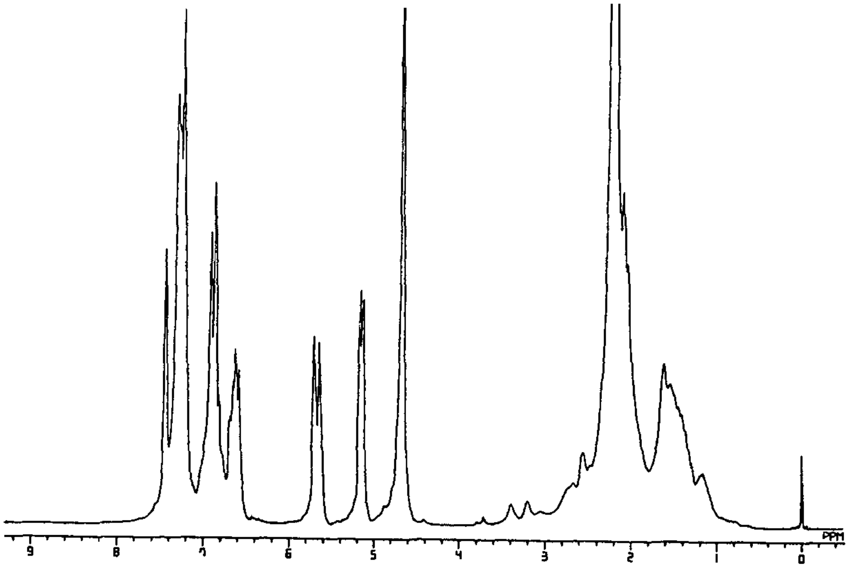


Figure 2 NMR for VBT monomer I, in $CDCl_3$-TMS

monomers(V-VIII) are thermally reactive. However, brominated monomers are slightly more reactive than the corresponding nonbrominated monomers.

Table 2. Reactivity of thermally reactive VBT monomers

Structure	T°C(by DSC)		Gel time at 175°C.
	onset	max.	
I	180	220	6-7min.
II	170	220	5min.
IV	180	220-230	9min.
V	160	200-210	3min.
VI	165-170	230	4-5min.
VII	160-170	240	4min.
VIII	160-170	200	3min

Thermal mechanical properties and thermal stability

Table 3 lists some representative thermal properties of the cured resins. Thermal mechanical analysis(TMA) was utilized to measure the glass transition temperatures(T_g) of the cured resins. The highly crosslinked network structure I with rigid fused ring on the backbone and structures VI-VII with metabrominated substituents on the aromatic rings have higher T_g.

Both thermogravimetric analyses(TGA) under nitrogen and isothermal gravimetric analyses(ITGA) at 250°C in circulating air indicated the significant difference in thermal stability among structures I-VIII due to varying the structures of polyphenols' backbones. The cured resin with structure I has excellent thermal stability. Only a slight weight loss was observed after aging at 250°C for 250 hrs. Bromine containing resins (V-VIII) are different in thermal stability. The cured resins of V-VII with ortho-methylation at the aromatic rings are more stable than VBT tetrabromobisphenol A(VIII). Moreover, the biphenyl structure in V and VI seems to play a major role in contributing to the thermal stability of structure V and VI , compared to the bis-F structure in VII and the bisphenol-A structure in VIII. These thermal properties provide important structural information for designing thermally stable VBT monomers and oligomers. It is of interest here to compare the thermal stability of cured resin of structure I having >99% phenolic OH conversion vs. only 94% phenolic OH conversion. Temperature at 5% weight loss for them is 415°C vs 355°C, a 60 °C difference.

Table 3. Some thermal properties of the cured resins with structure I-VIII

Structure	T_g	Dec.Temp.,°C (at 5% w_t.loss in N_2)	Isothermal Wt.Loss in% (250hrs/250deg.C)
I	209°C	415°C	1.66%
II	/	390	2.60%
IV	/	380	3.44%
V	/	380	3.89%
VI	213	385	12.81%
VII	214	355	15.05%
VIII	/	315	38.29%

Electrical properties and moisture absorption of the cured resins

Dielectric constant and dissipation factor of the cured resins measured at 10^3 Hz. are shown in **Table 4** and Resin with structure I has low dielectric constant through the range of 10^3-10^6Hz and less change in dielectric constant after moisture exposure. A slightly higher dielectric constant for structures VI and VII may be attributed to their unsymmetric backbone nature.

The phenolic OH conversion was also found to have an effect on the dielectric constant. Higher dielectric constants were observed for structures I and II when the conversion of the aromatic phenolic hydroxyl groups is below 95%.

Table 4. Dielectric constant/dissipation factor and moisture pick-up of the cured resins

Structure	Dielectric Constant at 10^3Hz /Dissipation Factor	Weight Gain in% (100hrs/boiling H_2O)
I	2.71/0.007	0.3%
II	2.82/0.003	0.5%
IV	2.84/0.003	0.4%
I+V	2.84/0.003	0.3%
VI	2.95/-	0.5%
VII	2.95/-	0.5%

The moisture resistance of all the cured resins with structures I-VIII is good. The weight gain of the test coupons of each cured system through 500 hrs. of exposure in boiling water is low. These results are attributed to the hydrophobic nature of the structures I-VIII.

General methods and synthetic procedure

Instrumentation probes and testing

Infrared spectra were recorded on a Nicolet 60SX FTIR spectrophotometer. The ^{1}H NMR and ^{13}·C NMR spectra were taken in $CDCl_3$ and determined on a JEOL JNM-GX 400 FTNMR spectrometer. Chemical shifts are in parts per million relative to $(CH_3)_4Si$ followed by the multiplicity of the signal in the parenthesis. Glass transition temperature and other thermal data were measured by using a DuPont 943 thermomechanical analyzer with a DuPont 1090 thermal analyzer. Thermal gravimetric analyses were conducted on a Perkin-Elmer TGS-2 system.The sample(approximately 10mg) were heated at 10°C/min. in a steady nitrogen stream of 35cc/min. The isothermal weight loss in air after 250hrs/250°C is based upon the numbers obtained from coupon of size 1"x2"x1/8". For determining the dielectric constants, coupons approximately 3"x3"x1/8" were cut from each clear casting and measured with the Gen Rad 1689 bridge and LD-3 cell. The weight gain due to moisture absorption was measured periodically at room temperature after immersing the clear casting into boiling water. The weight gain is based upon the average number obtained from the three coupons of size 1"x2"x1/8". The water on the surfaces of the coupons was carfully wiped off prior to weighing.

Synthesis of monomer I

The solvents and reactants were commercially available and were used without further purification. A commercial sample of an isomeric mixture of vinylbenzyl chloride(VBC) containing 40% para- and 60% meta- isomers was used as received from The Dow Chemical Co. Precursors for monomers I-VIII were provided by The Dow Chemical Co.

A 1000ml DMF solution containing 282g(0.75eq.) of dicyclopentadienyl bis-(2,6-dimethylphenol) was charged into a four necks 2l. flask equipped with a mechanical stirrer, thermometer, cooling condenser and addition funnel. 90g(2.25eq.) solid NaOH was then added at room temperature. The mixture was stirred under nitrogen for 4hrs. at 40-45°C and turned dark green in color when the formation of the sodium phenoxides was completed. After cooling to room temperature, 275g(1.8eq.) of VBC was added dropwise at 25-30°C over a period of 90min. Upon completion of the addition, the mixture was maintained at a temperature of 35°C for 4hrs. The mixture turned blue in color. After reacting at 45°C for another 2hrs., the precipitates were filtered and the solution was neutralized with dry ice. The solvent was removed by a rotating evaporator at 70-80°C under 10mmHg. Then 1000ml of toluene/methylethyl ketone mixture(25/75) was added into the syrupy residue. The solution was then washed with water (150-200ml/each) succesively. The organic layer was separated and concentrated under 5-10mmHg at 60-80°C. 390g of viscous liquid product(90% yield) were obtained without the need for further purification. Infrared spectrum of the product showed no residual phenolic OH absorption peak at 3200-3600cm^{-1}, two strong bands at 900 and 990cm^{-1} representing characteristic C-H bending vibration of vinylbenzyl double bonds. ^{1}H MNR(in $CDCl_3$): 2.25ppm(s.,12H); 1-2.75ppm(br., 14H); 4.72ppm(d., 4H); 5.0-7.7ppm (m., 18H,aromatic).

Clear casting preparation

Castings were made by heating thermally reactive monomers to 60-80°C, until they were completely melted. Degassing was carried out at <80°C under vacuum(<5mmHg) to remove entrapped air, then the resin was poured into a preheated mold(100°C). The resins were heated at 120-130°C for 1hr., 170-175°C for 2hrs., followed by 210-220°C for 2hrs.

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