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Summary

New epoxy resins containing azomethine groups were synthesized by condensation reaction A series of bis(azomethine)s were synthesized by reacting an aromatic diamines namely, 4,4'-diaminodiphenyl methane and 4,4'-diaminodiphenyl ether with 4-hydroxy-3-methoxybenzaldehyde and 4-hydroxybenzaldehyde in a 1 2 mole ratio to afford the corresponding bis(azomethine)s, and subsequent reaction with DGEBA in the presence of *n*–butylamine as catalysist to produce the epoxy resins The structures of bis(azomethine)s and epoxy resins were characterized and confirmed by FTIR, ^{1}H–NMR, UV and elemental analysis Thermal stability and degradation behavior of these epoxy resins were examined by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) The results of thermal analysis showed that, all resins possess good thermal stability The epoxy resins based on p–hydroxybenzaldehyde exhibited high thermal stability as compared to 4–hydoxy–3–methoxybenzaldehyde

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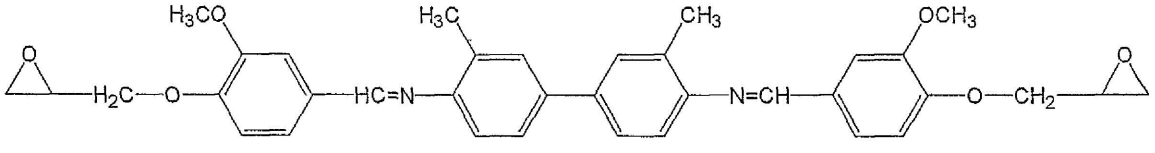
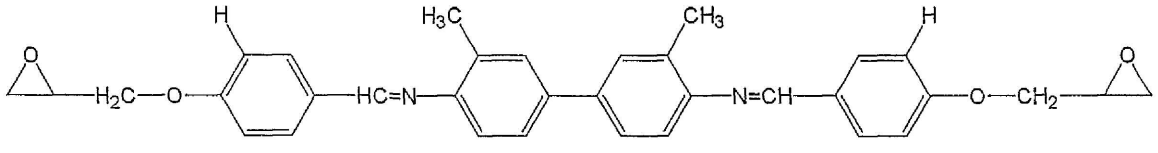
Epoxy resins are one of the most important classes of thermosetting materials and have been widely used in aerospace engineering, as an encapsulation compound for electronic industry and also as a matrix for coating, because of their characteristic properties such as strong bonding strength, high insulation resistances, good thermal and chemical resistance. However, there are disadvantages associated with processing as well as insolubility of these compound in common organic solvents There are two approaches to overcome this problem, first is to introduce flexible spacers in the backbone of the polymer Second approach is to obtain liquid crystalline properties

In our work, we synthesized new liquid crystalline epoxy resins containing azomethine linkages, which possess good thermal as well as mechanical properties They can be used as new materials for adhesives, coating as well as in electronic industry

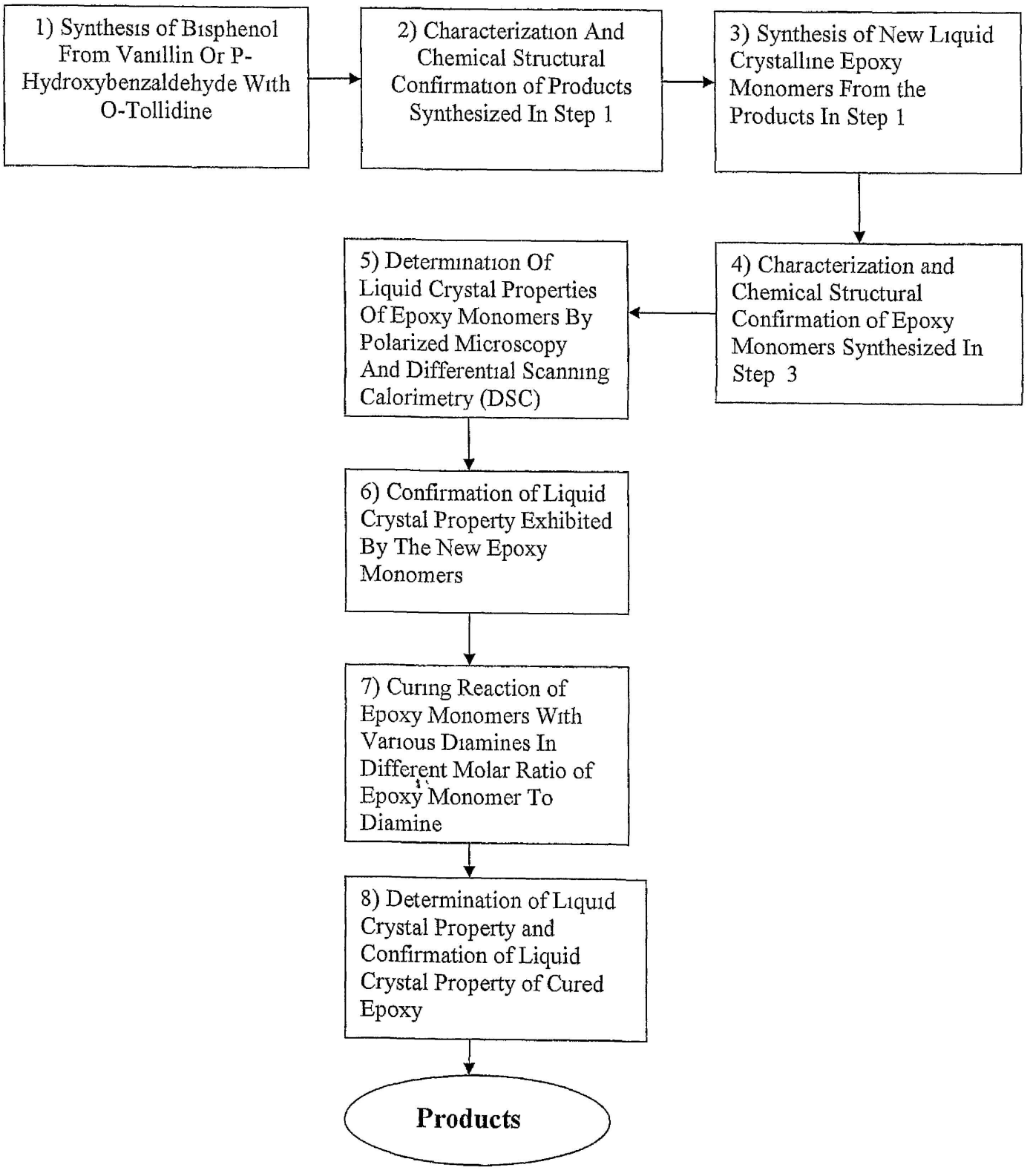


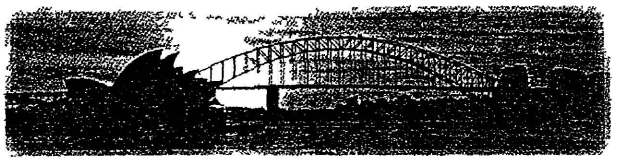
3,3' – dimethoxy – 4,4' – di (2,3-epoxypropoxy) – N- benzylidene – *O* – Tolidine



4,4' – di (2,3-epoxypropoxy) – N – benzylidene – *O* – Tolidine

Block Diagram of
The Overall Process Involved In
The Research Of Synthesizing New Epoxy Resin





COMPOSITES TECHNOLOGIES FOR *2020*

Proceedings of the Fourth Asian-Australasian Conference on Composite Materials (ACCM-4)

ACCM-4
Sydney 2004

University of Sydney, Australia

Edited by
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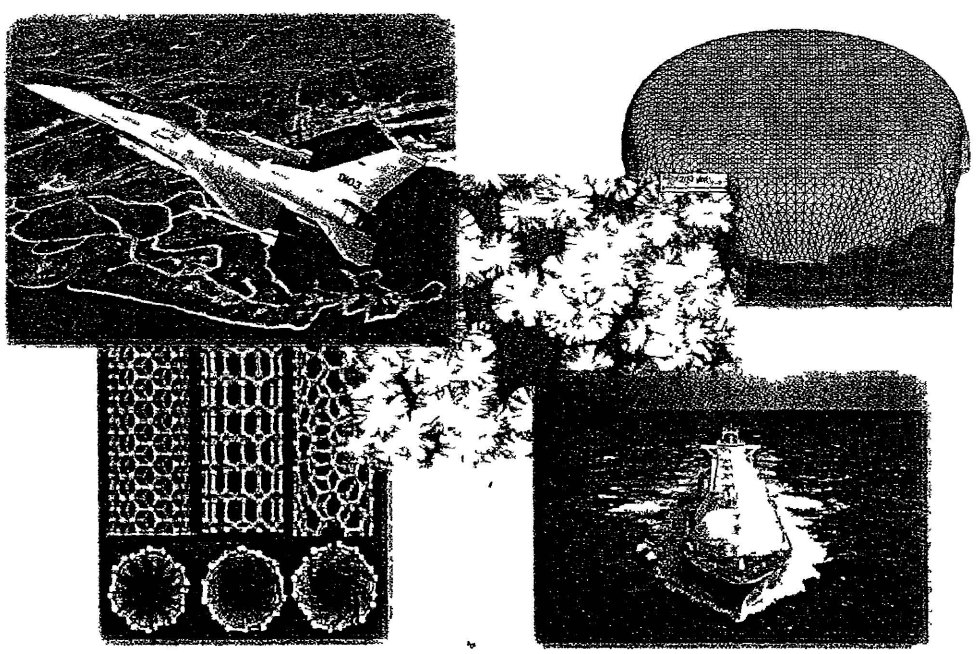

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Over the past three decades, composite materials have been gaining acceptance in a wide range of industries, competing with traditional structural and functional materials in meeting the demands imposed on high-performance structures Notable examples of breakthroughs based on the utilisation of composite materials can be found in transportation vehicles (aircraft, the space shuttle, automobiles), civil infrastructure (buildings, bridges, highway barriers), and sporting goods (Formula 1, golf clubs, sailboats), etc This increase in use has resulted from an improved understanding of the performance characteristics and application potential of composite materials as well as from innovative and cost-effective manufacturing processes

As the equivalent of the International Conference on Composite Materials (ICCM) in the Asian-Australasian regions, the Asian-Australasian Association for Composite Materials (AACM) has played a vital leading role in the field of composites science and technology since its inception in 1997 in Australia The theme of ACCM-4, held in Sydney, Australia, 6–9 July 2004, is Composites Technologies for 2020 ACCM-4 presents state-of-the-art achievements and recent advances in composites sciences and technologies, and discusses and identifies key and emerging issues for future pursuits By bringing together leading experts and promising innovators from the research institutions, end-use industries and academia, ACCM-4 intends to facilitate broadband knowledge sharing and to identify opportunities for long-term cooperative research and development ventures The scope of ACCM-4 is broad and includes, but is not limited to Bio-composites, Ceramic matrix composites, Durability and aging, NDE and SHM, Eco-composites, Manufacturing and processing technologies, Industrial applications, Interphases and interfaces, Impact and dynamic response, Matrices (polymers, ceramics, and metals), Mechanical and physical properties (fatigue, fracture, micromechanics, viscoelastic behaviour, buckling and failure, etc), Metal matrix composites; Multi-functional composites, Nano-composites, Reinforcements (textiles, strand, and mat), Smart materials and structures; Technology transfer (education, training, etc)

Professor Lin YE is full Professor and Head at the School of Aerospace, Mechanical and Mechatronic Engineering at the University of Sydney He is also Director of DSTO-AED Centre of Expertise in Damage Mechanics Over the years he has established strong expertise in the areas of composites science and technology, smart materials and structures, structural integrity and durability, nano-materials and nanocomposites **Professor Yiu-Wing MAI** is Australian Federation Fellow, Pro-Dean of Engineering and Director of the Centre for Advanced Materials Technology, the University of Sydney His research interest is in the field of science and technology of advanced materials, manufacturing processes, and fracture and fatigue mechanics **Dr Zhongqing SU** graduated with Bachelor of Science and Master of Engineering degrees from Beijing University of Aeronautics and Astronautics He completed his PhD study at the University of Sydney in 2004 and now works as a research associate His research interest is focused on smart materials and structures, structural health monitoring, signal processing and composites science

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New Epoxy Resins Based on Azomethine Groups for Potential Polymer Applications

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Universiti Sains Malaysia

ABSTRACT

A series of new epoxy resins containing azomethine groups were synthesized by condensation reaction The structures were characterized and confirmed by FTIR, ^{1}H–NMR, ^{13}C–NMR, UV and elemental analysis Thermal stability and degradation behavior of these epoxy resins were examined by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) The results of thermal analysis showed that, all resins possess high thermal stability The epoxy resins based on p–hydroxybenzaldehyde exhibited high thermal stability as compared to 4–hydoxy–3–methoxybenzaldehyde The resins produced showed good properties and can be used as matrix in polymer composites

INTRODUCTION

Epoxy resins are among the most important thermosetting polymers in wide use as a matrix for fiber–based composites, structural adhesives, surface coatings, etc [1,2] Most of the commercially available epoxy resins are oligomers of DGEBA [1–3] The epoxy resins are characterized by the presence of the oxirane group which is able to react with compounds possessing active hydrogen atoms, including amines, amides, or mercaptans Various glycidyl esters, glycidyl amine derivatives and thioethers have been synthesized using this approach [3,4]

The synthesis, characterization, and polymerization of epoxy resins of various glycidyl ethers and esters containing azomethine groups have already been reported [5–7] Owing to the relatively high thermal stability given by the presence of azomethine linkages [8–11], heat–resistant epoxides were prepared by reacting hydroxy and/or carboxy substituted azomethines or bis–azomethines with epichlorohydrin in the presence of a quaternary ammonium bromide as catalyst

The present paper deals with the synthesis of some new epoxy resin with azomethine linkages included in the main chain The products, obtained by the direct reaction between DGEBA epoxy resin and various azomethine bisphenols, were characterized by both spectral and thermoanalytical techniques, the results being related to the chemical structure of the synthesized polymers

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EXPERIMENTAL

Materials

P–phenylenediamine and ethylene diamine (Fluka Co) were used without further purification Vanillin, 4–hydroxy–3—methoxybenzaldehyde, p–hydroxybenzaldehyde and epichlorohydrine (Aldrich Co) were used without further purification

Preparation of Azomethine Bisphenols

Aldehyde (0 1 mol) was added dropwise to a solution of diamine (0 05 mol) in absolute ethanol The mixture was refluxed for 6 h with stirring in 500 ml flask to allow complete reaction, followed by precipitation, filtration and washing several times with diethylether The precipitate was finally dried for 24 h in a vacuum oven at 70 °C Final purification was carried out by re–crystallization from 1–butanol and then dried for 24 h in a vacuum oven at 75 °C

Preparation of the Epoxy Resins Containing Azomethine Groups

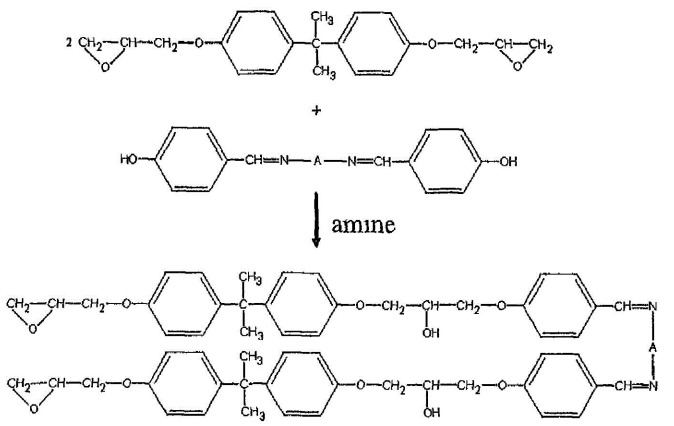
Preparation of the epoxy resins with azomethine groups in the main chain of the polymer was carried out in bulk using DGEBA epoxy resin and the azomethine compounds, synthesized as previously described The reagents, taken in the molar ratio DGEBA/azomethine of 2 1, were first heated at 100 °C for 1 hr, then *n*–butylamine, used as a selective catalyst for the ring opening of the epoxide compound [12], was added The mixture was stirred at 100 °C for 2–4 hr, and at 130 °C for 1 h to complete the polymerization process The product, obtained as a solid glassy resin, was purified by dissolution in acetone, filtered several times and precipitated in toluene Finally, the product was dried in vacuum at 80 °C for 10 h The yields ranged from 75 to 80%

Instrumentation

The FTIR spectra of the newly synthesized epoxy resins were recorded on Perkin Elmer 2000 ^{1}H–NMR spectra were obtained using Brucker 300 MHz NMR spectrometer in $CDCl_3$ as the solvent and TMS as the internal reference The glass transition temperature (T_g) was obtained by differential scanning calorimetry (DSC) by means of a Perkin Elmer DSC7 Series at a heating rate of 20 °C min^{-1} in a nitrogen atmosphere ₁The epoxy equivalent was evaluated by dissolution of the sample in pyridine (HCl) solution) and titration with aqueous NaOH solution in the presence of phenolphthalein, as previously described [13]

RESULTS AND DISCUSSION

The general reaction yielding the epoxy resins containing azomethine linkages is given in Scheme 1

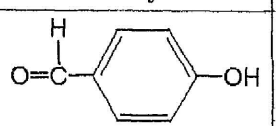
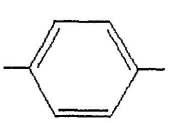
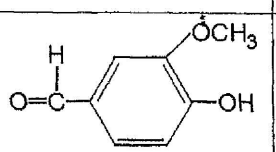
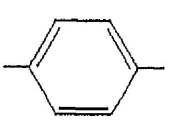
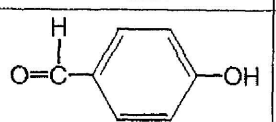
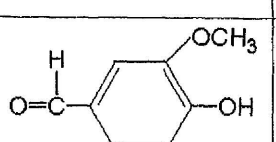


Scheme 1

The chemical nature of the A radical and elemental analysis of the synthesized epoxy resins are listed in Table 1

The ring opening of the epoxide compound (Scheme 1) is followed by the appearance of the secondary alcohol group [14–15]. The degree of the selectivity of the reaction depends on the active hydrogen compound used, on the catalyst and on reaction temperature The use of the selective amine catalyst and reaction temperatures higher than 90 °C determines a 100–fold increase in the epoxide–phenol reaction [13] The experimental conditions used and the experimental data obtained confirm the linear structure of the obtained epoxy resins containing azomethine

TABLE I Elemental analysis of the synthesized epoxy resins (1–4)

Sample	Aldehyde	A	C (%)	H (%)	N (%)
1			(11 23) 11 24	(11 23) 11 24	(11 23) 11 24
2			(11 23) 11 24	(11 23) 11 24	(11 23) 11 24
3		$-(CH_2)_2-$	(11 23) 11 24	(11 23) 11 24	(11 23) 11 24
4		$-(CH_2)_2-$	(11 23) 11 24	(11 23) 11 24	(11 23) 11 24

Values in brackets are calculated

The FTIR spectra of the epoxy resins containing azomethine linkages showed the presence of the characteristic absorption bands at 900, 1200, and 1250 cm^{-1}, attributed to the epoxy group The 575 – 585 cm^{-1} and 1120 cm^{-1} bands correspond to the vibration of the ether group ($-CH_2-O-C_6H_4-$), while the bands within the 1615 – 1635 cm^{-1} range assigned to the –CH=N– bond The bands indicating the presence of the aromatic ring are placed at 3100 and 1500 cm^{-1}, respectively

The ^{1}H–NMR spectra of the synthesized epoxy resins showed a singlet at 1 7 ppm, specific to the methylenic protons, a multiplet situated in the 2 6–3 8 ppm interval for the protons of the epoxy group, a multiplet observed in the 6 5–7 3 ppm interval for the aromatic protons and a singlet at 8 69 ppm, assigned to the azomethine protons Figure 1 shows a typical ^{1}H–NMR spectrum recorded for sample 1

The UV spectra of the epoxides showed absorption bands placed in the 330–360 nm interval (characteristic to the epoxy groups) Compounds with methoxy groups in the backbone **(2,4)** showed a little blue shift as compared to the compounds **(1,3)**

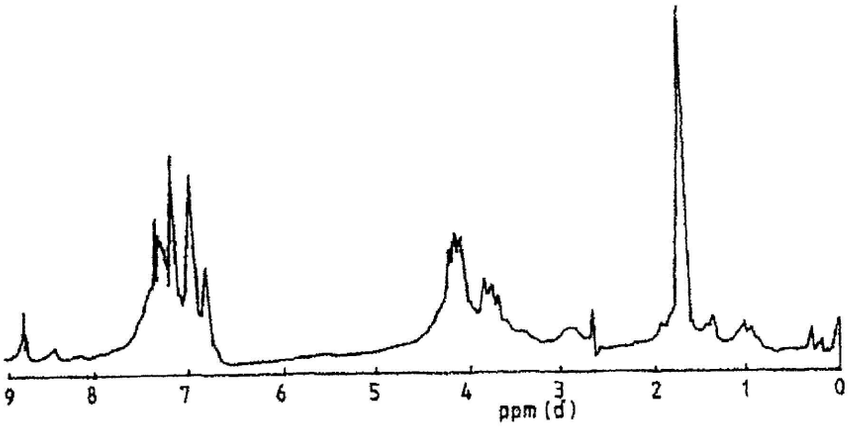


FIGURE 1 ^{1}H – NMR spectrum of Sample 1

The DSC curves recorded with repeated heating–cooling cycles allowed the evaluation of T_g values of the synthesized epoxy resin The T_g values are situated in the 35–60 °C temperature range It is obvious that they depend on the structure of the epoxides, T_g increasing with increasing polymer molecular weight [16]

One might expect the polymers with azomethine segments in the main chain to have high thermal stability The thermal behaviour of the synthesized epoxides was evaluated by dynamic TG experiments in nitrogen and air

Epoxides containing azomethine groups in the main chain showed an apparent thermal stability higher than that of the DGEBA epoxy resin The polymers **1** to **4** suffer a degradation starting from about 200 °C in air whereas about 250 °C in nitrogen An increased decomposition rate being observed in the 300–450 °C temperature range, when the weight losses reach about 60–70% The very close similarity of the thermograms suggests that the heat stability of the synthesized epoxy resin is not significantly influenced by the structure of the azomethines introduced in the main chain of the DGEBA resin Considering that the compounds incorporating azomethine groups (i e mesogenic units) and flexible spacers in the main chain could

possess both heat resistance and liquid crystalline properties [17–18], further investigations will concentrate on this aspect

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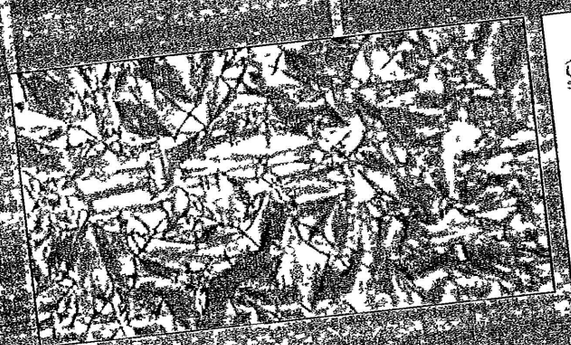

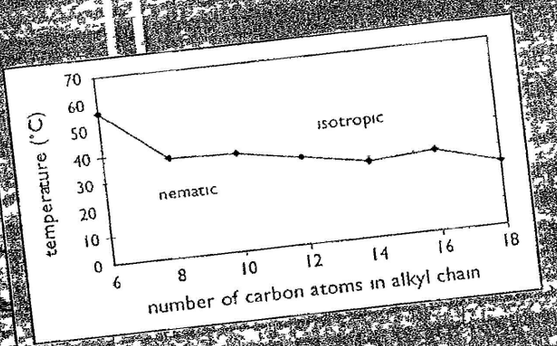

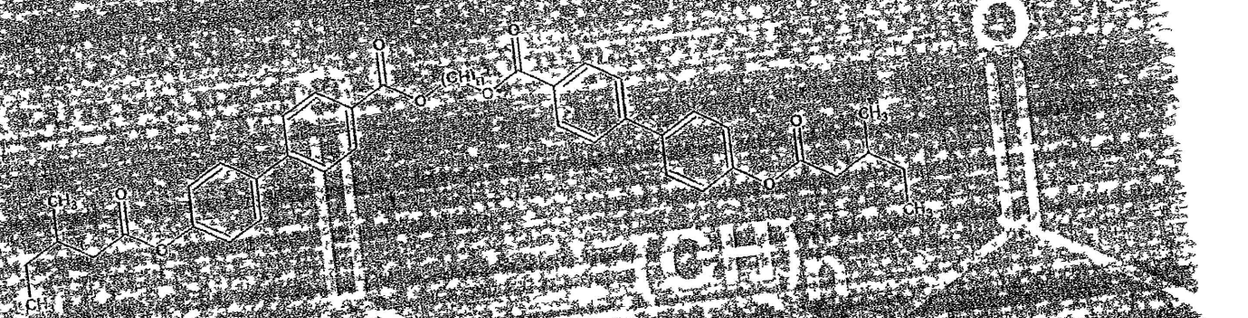

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LIQUID CRYSTALLINE TWIN EPOXY MONOMERS BASED ON AZOMETHINE MESOGEN: SYNTHESIS AND CURING WITH AROMATIC DIAMINES

Issam, A M and Lim, K W*

School of Industrial Technology, Universiti Sains Malaysia, 11800 Penang, Malaysia

New liquid crystalline (LC) epoxy monomers with twin mesogenic azomethines were synthesized to prepare LC thermosets. The epoxy monomers were characterized by CHN analysis, FTIR, ^{1}H, ^{13}C-NMR spectroscopy, thermogravimetic analysis (TGA), differential scanning calorimetry (DSC) and polarized microscopy (PLM) The epoxy monomers were found to form nematic phase in the melt Cure behavior of a stochiometric mixture of epoxy monomers with various aromatic diamines was investigated by DSC Nematic LC texture for the cured epoxy monomers was identified by polarized microscopy