Review Thermal and non-thermal interaction of microwave radiation with materials

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Industrial use of microwave radiation as an alternative to conventional thermal heating has generated interest recently mainly because of the drastic reduction in the processing time. In spite of its wide application, its chemical mechanism of interaction with materials has not been well understood. The current debate on the alternative use of microwave radiation to conventional thermal heating is on the involvement of a "microwave specific effect" other than the well accepted dielectric heating. There are reports of various reactions which show similar kinetics under both microwave and thermal methods at similar temperatures suggesting simple dielectric heating of materials by microwaves. There are also reports which show a clear reaction rate enhancement under microwave radiation compared to the thermal method under similar reaction conditions and temperatures indicating a "microwave specific effect" other than the simple dielectric heating of materials. This paper will discuss the above conflicting results reported in the literature.

1. Introduction

The microwave region of the electromagnetic spectrum corresponds to waves of wavelength 1 mm to 1 m (frequencies of 300 GHz to 300 MHz respectively). Domestic and industrial microwave ovens generally operate at a wavelength of 2.45 GHz corresponding to a wavelength of 12.2cm and energy of 1.02×10^{-5} eV. A material can be heated by applying energy to it in the form of microwaves which are high frequency electromagnetic waves. The electric field component of microwaves exerts a force on the charged particles found in the compound. If the charged particles are able to move freely through the electrical field, a current is induced. However, if the charged particles are bound in the compound, restricted in their movements, they merely reorient themselves in phase with the electric field. This is termed dielectric polarization. The dielectric polarization can be made up of four components [1] based on the different types of the charged particles in matter: electrons, nuclei, permanent dipoles and charges at interfaces

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\alpha_t = \alpha_e + \alpha_a + \alpha_d + \alpha_i \qquad (1)
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where α_t = total dielectric polarization, α_e = electronic polarization due to polarization of electrons surrounding the nuclei; α_a = atomic polarization due to polarization of the nuclei; α_d = dipolar polarization due to polarization of permanent dipoles in the material; and α_i = interfacial polarization due to polarization of charges at interfaces.

The electric field reversal of the microwave radiation causes the reversal of the dielectric polarization. The atomic and electronic polarization and depolarization occur at a faster time scale than the electric field reversal of a microwave and therefore do not contribute to the dielectric heating effect. (The resonant frequency of the electronic and atomic polarization is in the ultraviolet/visible and infrared frequency, respectively.) The time scale of orientation and disorientation of permanent dipoles in a molecule is similar to the time scale of electric field reversal in the microwave region. In the microwave region, therefore, the dipoles rotate to align themselves in phase with the reversing electric field. The resulting polarization lags behind the changes of the electric field and causes dielectric heating of the material. The extent of this dipolar polarization depends on the power of the field, strength of the dipole moment, and the mobility of the dipole. The interfacial polarization contributes to dielectric heating when conducting particles are suspended in a non-conducting medium in an inhomogeneous material. Thus both conduction and dielectric polarization are vehicles of microwave heating in matter.

The use of microwave radiation as an alternative to the conventional thermal curing method has increasingly been applied to the industry and extended

recently to the area of chemical synthesis and study of various chemical reactions. Even though microwaves have found a wide application, its chemical mechanism of interaction with the irradiated material has not been well understood. In the field of microwave catalysis, microwaves have been shown to interact selectively with different materials. A suitable material which would absorb the microwaves strongly, called a sensitizer, is usually selected which would preferentially absorb the microwave energy and pass it on to other substances to initiate a chemical reaction. This concept has been used as a basis for initiating and controlling catalytic reactions E2-9]. The desired chemical selectivity in the products is typically achieved by appropriate microwave pulsing. In the field of MORE chemistry (microwave oven induced reaction enhancement), polar molecules have been shown to absorb microwaves strongly in comparison to non-polar molecules [10, 11]. To bring about a rapid reaction in the microwave oven, therefore, the choice of the solvent is critical. Such specific interaction of microwaves is well accepted. However, "microwave specific" activation has been a debated concept which actually refers to a unique interaction, reaction or activation, specific to the microwave radiation. Reactions which otherwise would take hours or even days to complete with conventional heating methods have been shown to be completed in significantly less time by using microwave radiation [12, 13]. A satisfactory explanation of this microwave phenomena has not been reported so far. Two proposed models of the chemical mechanism have emerged from research work done so far on microwave induced reaction enhancement chemistry. The first proposed mechanism assumes that whilst the reaction time is drastically reduced in a microwave induced reaction, the kinetics or mechanism of the reaction is not altered. The temperature of the system is greatly enhanced on microwave irradiation resulting in a dramatically increased rate of reaction. The proposal assumes that the reaction rate enhancement is simply due to this thermal dielectric heating effect. The alternative proposal assumes that there is a specific activation effect due to microwave radiation that is acting in addition to the dielectric heating mentioned earlier. This is also referred to as the non-thermal effect of microwaves. One of the main complications associated with the microwave induced reaction has been the fact that microwaves usually induce dielectric heating in the irradiated material. This of course would give rise to a thermally induced reaction.

2. Thermal activation of microwave radiation

Gedye *et al.* [11, 14] have observed that organic reactions carried out in sealed Teflon containers in a microwave oven showed reaction rate enhancements of 10 to 1200 times compared to conventional methods. An inverse relationship between rate enhancement and the boiling point of the solvent was demonstrated in a series of esterification reactions. The reaction rate was shown to be directly proportional to the pressure developed within the vessels in the preparation of 4-cyanophenyl benzyl ether. Giguere *et al.* [15, 16] observed a similar reduction in reaction times in many organic reactions using a microwave oven. Baghurst and colleagues [17] also demonstrated a reduction in synthesis time of organometallic compounds in a microwave autoclave. The rhodium (I) and iridium (I) dimers which are used as starting material for organometallic synthesis are generally prepared by reftuxing the reagents in alcohol-water mixtures for 4-36 h. In a microwave autoclave, the same reaction was shown to give a good yield of the products in less than one minute. The rate enhancement was thought to be due to the high pressure and temperature created within the sealed vessels.

For a better comparison of microwave and thermal reactions, identical conditions have to be maintained in both the methods. Controlling and measuring temperature in the microwave oven is a major complication in microwave radiation, as the electric field induced can cause serious errors in thermocouples used to measure the temperature, unless they have been carefully designed. This difficulty arises due to three reasons, namely electromagnetic interference, direct heating of the sensor, and perturbation of the field by the thermometer. The problem due to electromagnetic interference can be eliminated by placing the sensor perpendicular to the field. Direct heating and perturbation of the sensor can be avoided by using a low dielectric loss material such as an optical fibre [18].

Due to this difficulty in measuring temperature in a microwave oven, Bond *et al.* [19] did not measure the temperature. To conduct experiments under identical temperature and pressure, they studied the acidcatalysed esterification of propan-l-ol with ethanoic acid at reflux temperature and atmospheric pressure. Microwave irradiation was then carried out in a multimode, variable power output microwave oven, suitably modified to accommodate refluxing of the solvent. Concentration of ester as a function of time was similar under both microwave and conventional conditions. They conclude, however, that for the particular system all reactants and products were strong absorbers of microwave radiation and therefore no specific rate effect was seen.

The cycloaddition of anthracene and dimethylfumarate in trichlorobenzene was carried out in a microwave oven and the reaction temperature was deduced by placing melting-point capillaries filled with various substances [20]. The substances in the capillaries which melted at their melting points gave the temperature of the reaction in the microwave oven. For comparison, the same reaction in an oil bath at $190-200^{\circ}$ C gave a similar yield to the microwave oven reaction and no rate enhancement could be established in the microwave oven. Similar results were obtained from the study of reactions involving carbonyl enophiles [21]. The reactions of diethylmesoxalate with 1-decene and beta-pinene, and cyclization of $(+)$ -citronellal under homogeneous and heterogeneous conditions were studied at the same bulk temperature and pressure. A Luxtron optical fibre thermometer was used to measure the temperature of the sample in the microwave oven. The dependence of reaction yield on time and the stereo-isomer ratio of the products were unaffected by the heating mode.

Jahngen *et al.* [22] have shown by infrared imaging that a large temperature gradient $(30^{\circ}C)$ exists in the microwave irradiated sample. Hence accurate temperature measurement is essential. Microwave irradiation was conducted in a multimode microwave system with adjustable power output. They determined the reaction kinetics of ATP (adenosine triphosphate) hydrolysis in the conventional heating method and calculated the Arrhenius parameters. Knowing the Arrhenius parameters and temperature, the concentrations of the reaction products can be predicted. Taking into account the temperature gradient, they predicted the concentration of product formed at a particular temperature in the microwave oven and found their prediction in agreement with the measured concentration of the reaction products in the microwave irradiated sample. They concluded, therefore, that the rate enhancement which they initially reported [23] was due to incorrect temperature measurement and that the rate enhancement was purely due to thermal reasons.

Similar to the above group, Raner *et al.* [24, 25] determined the reaction kinetics and the Arrhenius parameters of the acid catalysed esterification of 2,4,6 trimethylbenzoic acid in 2-propanol by the conventional heating method. Using these parameters, they predicted the concentration of the reaction products in the microwave oven at a particular temperature and found their prediction to hold true. The observed reaction rate in the microwave reactor was the same as that calculated from the Arrhenius parameters determined in the oil bath experiments. They also studied the acid catalysed isomerization of carvone to carvocol and the Diels-Alder reaction between anthracene and diethyl maleate reactions at the same temperature by the conventional heating method and microwave irradiation. Rate constants at several temperatures were measured and the activation parameters were determined under both conditions and the data compared. The rates of the reactions were similar under both conditions. All the above data which is summarized in Table I suggest that conditions being the same, there was no reaction rate enhancement in the microwave oven compared to the conventional methods and, therefore, microwave irradiation does not cause any change in the kinetics of the reaction.

3. Non-thermal interaction of microwave radiation

Reports of reactions which support the "microwave specific" activation could be classified under the following six categories and are summarized in Table II.

3.1. Reaction rate enhancement due to "hot spots"/Iocalized heating effects

Reaction rate enhancement as high as 300 times were observed in the synthesis of long chain alkyl acetates on alumina in a dry medium using a commercial microwave oven $[26]$. The authors noted that where supported reactions are concerned, simple dielectric heating may not be sufficient to explain the observed reaction rate enhancement. Lewis et al. [27] studied the cure kinetics of polyimides by conventional and microwave heating. The extent of the reaction was followed by Fourier transform infrared spectroscopy (FT-IR). A 34-fold rate enhancement at 160° C, and a 20-fold rate enhancement at 170° C was reported. This group also studied the curing of an epoxy system, DGEBA (diglycidyl ether of bisphenol A) and DDS (diaminodiphenyl sulphone) resin [281. The temperature of the resin during the microwave cure was continuously monitored using a fibre-optic probe. The thermal cure was followed at a comparable temperature and 8-10-fold decrease in cure time for 100% completion of the reaction was observed in the microwave cure. The authors suggest that a localized superheating effect may be the reason for the observed rate enhancement of microwave irradiation.

Marand *et al.* [29, 30] monitored the isothermal polymerization of epoxy materials (DGEBA and

TABLE II Summary of literature supporting microwave rate enhancement under comparable thermal and microwave conditions

DDS) at temperatures that ranged from 140–200 °C *in situ* and followed the changes in dielectric properties and infrared spectra. Using the cavity perturbation method, a sample in the wave guide was cured via a microwave generator or hot N_2 gas, while its dielectric constant was periodically measured using infrared optical fibres. The infrared spectrum of the sample was measured *in situ* under both microwave radiation and thermal heating by remote sensing fibres. They found that the rate of cross-linking is much higher in microwave cured sample compared to that cured thermally. This induced rapid cross-linking apparently created a molecular network which was rigid enough to trap unreacted functional groups, thus actually causing a lower degree of cure as observed earlier by Mijovic *et al.* [31-33]. Marand and co-workers have suggested two possible reasons:

(i) The reactive polar molecules absorb microwaves selectively enhancing the reaction quickly while in the conventional method, the whole molecule has to be heated before the reaction could take place.

(ii) In general, secondary amines are less reactive than primary amines due to steric reasons. Under microwave irradiation, secondary amines absorb microwave energy causing inversion of the molecule similar to primary amines and the reactivities of the two amino groups become identical. In the microwave cured sample, therefore, the enhanced cross-linking is due to accelerated reaction of the secondary amine group.

The microwave curing of DGEBA and DDS resin on glass fibre matrix also resulted in a reaction rate enhancement [34, 35]. The thermally cured composite at 110 $\rm{^{\circ}C}$ for 10 h and postcured at 125 $\rm{^{\circ}C}$ for 4 h, yielded a polymer with glass transition temperature (T_g) of 111 °C. A polymer of similar T_g was obtained for microwave cured composites within 13-20 min depending on the power of the microwave radiation used. A high moisture content within the microwave cured sample, however, was found to have increased the time taken for maximization of the T_g and significantly increased the void percentage during the curing process [36]. Also, charring was observed at high powers (800 W) of microwave radiation [34]. Similarly, in the microwave curing of DGEBA/3DCM (4, 4'-diamino-3,3'dimethyldicyclohexyl methane), higher power resulted in oxidation and degradation of the samples [37]. The glass composite of the above sample was also studied, and uniform curing was observed for microwave cure of large size samples (2o-25 cm) [38].

Berlan *et al.* observed reaction rate enhancement in some Diels-Alder reactions along with selectivity in the cyclic trimerization of urea [39, 40]. The rates of the reactions were compared under similar bulk temperatures in the conventional and microwave (monomode wave guide) methods. The authors suggested that the bulk temperature of the reaction mixture may not be representative of the reaction conditions and similar to "hot spots" in sonochemistry; the microwave activation could be due to hot spots generated by dielectric relaxation on the molecular scale. Baghurst *et al.* [12] found that organometallic synthesis in a suitably adapted microwave oven to allow refluxing of the solvent within the microwave cavity showed a reaction rate enhancement of 6-40 times compared to the conventional refluxing method. The acceleration of the reaction by microwave radiation has been suggested to be due to either of the following reasons: superheating effects due to the presence of large number of ions present, superheating effects at the boundary between non-miscible liquids along with efficient mixing of reactants, and rapid achievement of the reaction temperature caused by microwave dielectric effects.

3.2. Reaction rate enhancement due to molecular agitation

Microwaves cause rapid shift of the dipoles found in the molecules of a compound. The intermolecular bonds hinder the rotation of the dipoles causing a lag in the dipoles following the electromagnetic radiation. This is explained as the reason for the heating effect observed on irradiating a compound with microwaves. This process may also be viewed as molecular agitation or stirring. Chen *et al.* [41] have shown that microwave irradiation could replace mechanical stirring in the synthesis of refractory b-branched amino acids. The yield of peptides was shown to be enhanced ~8-fold in microwave irradiation. This higher efficiency is attributed to both temperature elevation and perturbation in the molecular dipole moments induced by microwaves. They propose that the molecular agitation or stirring caused by microwaves could account for the non-thermal effect of microwaves.

3.3. Reaction rate enhancement due to improved transport properties of molecules

The slowest step in solid state reactions is the diffusion of reactants towards one another through an unreactire medium. Since the rate of a reaction is controlled by the slowest step, any process which could enhance the diffusion of reactants can lead to a significant rate enhancement. Research on microwave processing of ceramic component materials suggest that transport properties are enhanced on microwave irradiation. The diffusion of various cations in Pyrex glasses [42] and ethylene oxide (EO) in polyvinyl chloride (PVC) [43] have been studied by conventional and microwave heating. Microwave irradiation was shown to enhance the diffusion of reactants in both the above experiments compared to conventional heating at the same temperature or less. The mode of action of microwaves on the reactants was studied by examining the desorption of EO from PVC. It is suggested that enhancement in diffusion of EO in PVC on microwave irradiation is due to active disruption of hydrogen bonding between EO and PVC. The microwave synthesis of ceramic oxides were shown to occur in a fraction of the time taken by the conventional synthesis [44, 45].

Hedrick and colleagues [46] studied the microwave induced cross-linking of polyamylene ether ketone (PEK) containing end groups such as amine, maleimide and nadimide. Thermal cure was also performed in a conventional oven at the same temperature as used in the microwave oven. The time taken to reach a certain percentage of gelation, which was determined by Soxhlet extraction after 72 h, was used for kinetic evaluation. They reported a 20-fold decrease in curing time for maleimide-terminated PEK when irradiated with microwaves. This reduction in curing time was suggested as being due to significant increases in the rate of diffusion of reactive species. A similar rate enhancement was reported for the microwave curing of thin films of DGEBA/DDS and DGEBA/mPDA (metaphenylenediamine) system $\lceil 47, 48, 49 \rceil$. The microwave cure was shown to be sensitive to the curing agent used. A higher reaction rate enhancement was observed for the DDS system compared to the mPDA system. The microwave cure resulted in a higher T_g of the polymer formed compared to the thermally cured polymer. The T_{g} , however, was similar to the thermally cured polymer at lower conversions. The authors suggested an increase in the reactant mobility after gelation to be a factor causing the observed reaction rate enhancement. The gel effect of methylmethacrylate (MMA) cure was shown to be affected by microwave irradiation [50]. The gel effect also known as the Tromsdorf effect, the Norrish-Smith effect or the auto-acceleration of reaction, is well documented as being a diffusion controlled process [51]. At the gel effect, experimental results and theoretical predictions support the increase in molecular weight of the polymer formed [52, 53]. The microwave cure of MMA, however, showed a decrease in molecular weight of the polymer formed at the gel effect which is shown in Fig. $1 \mid 54$. This observation may be due to the effect of microwave radiation on the diffusion controlled process of gel effect.

3.4. Reaction rate enhancement due to other reasons

Bose *et al.* [55] have stated that MORE chemistry is not due to thermal heating. They conducted their experiments at atmospheric pressure and low power settings using a commercial 2.45 GHz microwave oven. To demonstrate that no thermal heating was involved, they placed the reaction vial in a block of ice and microwaved the sample together with the block of ice. Analysis of the sample after 3 min of microwave irradiation showed the formation of the desired product in good yield. This result therefore contradicted the reasoning that microwave reaction enhancement is due to simple thermal reasons. Jullien and co-workers [56] have noted that the highest temperature reached was not a function of the conversion rate. Specific pulsing of the microwaves led to high conversion rates. Also, using 13 C nuclear magnetic resonance (NMR) it was found that pulsed microwave radiation with a low repetition period of microseconds induced

Figure 1 Change in molecular weight of polymethylmethacrylate under microwave and thermal cure. Number average molecular weight, $\&$ 69 °C; **iii** 200 W. Weight average molecular weight, \Box 69 °C; \Leftrightarrow 200 W.

homopolymerization of DGEBA and DDS systems forming ethers while a longer pulse repetition period of 50 us promoted the reaction with amines only [57-59]. A similar correlation between the microwave pulse and chemical reaction was reported for the cross-linking reaction of DGEBA with DDM (diaminodiphenylmethane). These observations show that the extent of a chemical reaction on irradiation with microwaves is not related purely to the temperature rise in the sample.

3.5. Product selectivity due to microwave irradiation

Product selectivity on microwave irradiation has been reported for few reactions. The Diels-Alder reaction of 6-dimethoxy-b-dihydrothebaine with excess methylvinylketone gave extensive polymerization product under conventional conditions while using microwave irradiation, the desired adducts were obtained with less of the polymeric material [60]. Aloum *et al.* [61] have conducted a number of dry organic reactions, a high yield of the desired product was observed on microwave irradiation while the same dry reaction heated conventionally yielded only a trace amount of the desired product. For example, acetylene alcohol adsorbed on KSF clay (acidic montmorillonite type phyllosilicate) gave the desired rearranged product in 95% yield after 5 min of microwave irradiation. The same reaction heated to 170° C (which was attained just after microwave irradiation) conventionally for 5 min gave only 2% of the rearranged product. A specific microwave effect has also been shown in the cracking of neopentane on zeolites [62]. On microwave irradiation more methane is produced from neopentane than when heated in a classical furnace. A similar observation was reported in the reactions of methyl-2-pentane on a Pt/Al_2O_3 catalyst bed [63]. Microwave irradiation improved the production of benzene compared to conventional heating.

3.6. Superior mechanical properties on microwave irradiation

The literature on microwave specific activation seems to have focused largely on the reaction rate enhancement and there are very few reports comparing the morphological and mechanical properties of the microwaved sample with the conventionally treated sample. Karmazsin *et al.* [64, 65] have shown that the Young's modulus of a commercial epoxy resin AY103 and hardener HY991 polymerized for 600 s in a 75 W, TE_{10} wave guide (temperature less than 373 K) was more than 10% higher than the same resin polymerized at 373 K for 1 h in a conventional resistance furnace. Singer *et al.* [66] compared the values of tensile strength and Young's modulus of an epoxy-amine system cured by microwave irradiation and by conventional means. The microwave oven used was a cylindrical brass cavity resonating in the TE_{111} mode. Their finding was that the microwaved sample had a slightly higher Young's modulus and significantly lower tensile strength. Similarly, the microwave

processing of Hercules AS4/3501-6 composites resulted in improved mechanical properties compared to the thermally processed sample under similar processing conditions [67]. Boey *et al.* [68] showed that the interfacial strength of epoxy-glass composite (DGEBA/DDS system) cured by microwave radiation at 175 W reached a maximum interfacial strength of 20 MPa in less than 20 min while the thermal cure at 120° C for 12 h resulted in an interfacial strength of only 15 MPa. The microwave cure at a higher power of 275, 400 and 500 W resulted in greater interfacial strength in lesser time. The continuous irradiation of the sample at higher powers (400 and 500 W), however, resulted in the degradation of the polymer and optimization of the process was required to avoid overheating of the sample. The modulus value of the microwave cured sample was found to be higher than the thermally cured sample [69]. Microwave curing of carbon fibre composite has also been reported to result in improved interfacial strength [70]. The microwave sintering of ceramic samples of $TiB₂$ and 3% CrB₂ was reported to result in increased hardness and fracture toughness compared to the conventionally treated samples [71].

4. Conclusions

Interaction of microwave radiation with materials cannot be treated as a simple substitute for the conventional thermal method of heating. Its effect with regard to all the properties of the irradiated material has to be verified. It is highly possible that the properties of the irradiated material may not be similar to the conventionally treated material. Research work on the chemical interaction of microwave radiation with materials so far points to the following mechanisms of activation: by hot spots, molecular agitation, and improved transport properties of molecules.

References

- 1. D.M.P. MINGOS and D. R. BAGHURST, *Chem. Soc. Rev.* 20 (1991) 1.
- 2. Y. M. TSE, C. M. DEPHEW and J. K. S. WAN, *Res. Chem. Intermed.* 13 (1990) 221.
- 3. T.R.J. DINESEN, M. Y. TSE, M. C. DEPEW and J. K. S. WAN, *Ibid.* 15 (1991) 113.
- *4. K.L. CAMERON, M.C. DEPEWandJ. K.S. WAN, Ibid. 16* (1991) 5.
- 5. M.C. DEPEW, S. LEM and J. K. S. WAN, *Ibid.* 16 (1991) 213.
- 6. J.K.S. WAN, G. BAMWENDA and M. C. DEPEW, *Ibid.* 16
- (1991) 241. 7. J.K.S. WAN, *Ibid.* 19 (1993) 147.
- 8. J.K.S. WAN, M. Y. TSE, H. HUSBY and M. C. DEPEW, J. *Microwave Power Electromag. Energy* 1 (1990) 25.
- 9. G. BAMWENDA, E. MOORE and J. K. S. WAN, *Res. Chem. lntermed.* 17 (1992) 243.
- 10. R. N. GEDYE, F. E. SMITH and K. C. WESTAWAY, J. *Microwave Power and Electromag. Energy* 26 (1991) 3.
- 11. R.N. GEDYE, F.E. SMITH and K.C. WESTAWAY, Can. J. *Chem.* 66 (1988) 17.
- 12. D. R. BAGHURST and D. M. P. MINGOS, *J. Organomet. Chem.* 384 (1990) C57.
- 13. P. AYSOLA, P. D. ANDERSEN and C. H. LANGFORD, *Anal. Chem.* 21 (1988) 2003.
- 14. R.N. GEDYE, F. E. SMITH, K. L. WESTAWAY, H. ALI, L. BALDISERA, L. LABERGE and J. ROUSELL, *Tetrahedron Lett.* 27 (1986) 279.
- 15. R. J. GIGUERE, T. L. BRAY, S. M. DUNCAN and G. MAJETICH, *Ibid.* 2'7 (1986) 4945.
- 16. R.J. GIGUERE, A. MAMEN, B. LOPEZ, A. AREPALLY, D. RAMOS, G. MAJETICH and J. *DEFAUW, Ibid. 28(1987)* 6553.
- 17. D.R. BAGHURST, D. M. P. MINGOS and M. J. WATSON, *J. Organomet. Chem.* 368 (1989) C43.
- 18. M. A. STUCHLY and S. S. STUCHLY, *IEEE proceedings* 130(8) (1983) 467.
- 19. S. D. POLLINGTON, A. BOND, R. B. MOYES, D. A. WHAN, J. P. CANDLIN and J. R. JENNINGS, *J. Org. Chem.* 56 (1991) 1313.
- 20. A.K. BOSE, M. S. MANHAS, M. GOSH, M. SHAH, A. A. CHANDHARY and K. J. BARAKAT, *Ibid.* 56 (1991) 6968.
- 21. R. RAURENT, A. LAPORTERIE, J. DUBAC, J. BERLAN, S. LEFEUVRE and M. AUDHUY, *Ibid.* 57 (1992) 7099.
- 22. E.G.E. JAHNGEN, R. R. LENTZ, P. S. PESHECK and P. H. SACKETT, *Ibid.* 55 (1990) 3406.
- 23. w. SUN, P. M. ANY, J. H. JAHNGEN, R. F. ROS-SOMANDO and E. G. E. JAHNGEN, *Ibid.* 53 (1988) 4414.
- 24. K.D. RANER and C. R. STRAUNS, *Ibid.* 57 (1992) 6231.
- 25. K.D. RANER, C. R. STRAUNS, F. VYXOC and L. MOK-BEE, *Ibid.* 58 (1993) 950.
- 26. G. BRAM, A. LOUPY, M. MAJDOUB, E. AUTIEREZ and E. RUIZ-HITZKY, *Tetrahedron* 46 (1990) 5167.
- 27. D. A. LEWIS, T. C. WARD, J. S. SUMMERS and J. E. McGRATH, *J. Polym. Sci. Chem.* 30 (1992) 1647.
- 28. D. A. LEWIS, J. C. HEDRICK, T. C. WARD and J. E. McGRATH, *Polymer Prepr.* 28(2) (1987) 330.
- 29. K.R. BAKER, E. MARAND and J. D. GRAYBEAL, *PMSE* 66 (1992) 422.
- 30. E. MARAND, K. R. BAKER and J. D. GRAYKEAL, *Macromolecules* 25 (1992) 2243.
- 31. J. MIJOVIC and J. WIJAYA, *Ibid.* 23 (1990) 3671.
- 32. J. MIJOVIC, A. FISHBA1N and J. WIJAYA, *Ibid.* 25 (1992) 979.
- 33. *ldem., ibid.* 25 (1992) 986.
- 34. F.Y.C. BOEY and W. L. LEE, *J. Mater. Sci. Lett.* 9 (1990) 1172.
- 35. F. BOEY, I. GOSLING and S. W. LYE, *J. Mater. Proc. Teehn.* 29 (1992) 311.
- 36. F.Y.C. BOEY, *PMSE* 66 (1992) 422.
- 37. C. JORDAN, J. GALY, J. P. PASCAULT and M. DE-LMOTTE, *Ibid.* 66 (1992) 380.
- 38. L. OUTIIFA, H. JULLIEN and M. DELMOTTE, *ibid.* 66 (1992) 424.
- 39. J. BERLAN, P. AIBOREAU, S. LEFEUVRE and C. MARC-HAND, *Tetrahedron Lett.* 32(21) (1991) 2363.
- 40. J. BERLAN, K. CANN-PAILLER, J. IMBERT and R. TEISSIER, French Patent 0114720, 28.11, 1991.
- 4l. S. T. CHEN, S. H. CHIOU and K. T. WANG, *J. Chinese Chem. Soc.* 38 (1991) 85.
- 42. T.T. MEEK, R. D. BLAKE, J. D. KATZ, J. R. BRADBURY and M. H. BROOKS, *J. Mater. Sci. Lett.* 7 (1988) 928.
- 43. C. GIBSON, I. MATTHEWS and A. SAMUEL, *J. Microwave* Power Electromag. Energy 23 (1988) 17.
- 44. D. R. BAGHURST, A. M. CHIPPINDALE and D. M. P. MINGOS, *Nature* 332 (1988) 311.
- 45. D.R. BAGHURST and D. M. P. MINGOS, *J. Chem. Soc. Chem. Commun.* (1988) 829.
- 46. J.C. HEDRICK, D. A. LEWIS, G. D. LYLE, S. D. WU, T. C. WARD and J. E. McGRATH, *PMSE 60* (1989) 438.
- 47. J. D. DELONG, J. JOW and M. C. HAWLEY, in AIChE Second Topical Conference on Emerging Technologies in Materials, San Francisco, CA, Nov. 6-9, 1989.
- 48. J. WEI, M. C. HAWLEY, J. D. DELONG and M. DE-MEUSE, *Polym. Eng. Sei.* 33 (1993) 1132.
- 49. J. WEI, M. C. HAWLEY and M. T. DEMEUSE, *PMSE* 66 (1992) 478.
- 50. J. JACOB, L. H. L. CHIA and F. Y. C. BOEY, *Polym. Testing,* in press.
- 51. *A.M. NORTHandG. A. REED,J. Polym. Sci. 41(1963) 1311.*
- 52. S.T. BALKE and A. E. HAMIELEC, *J. Appl. Polym. Sci.* 17 (1973) 905.
- 53. J.N. CARDENAS and K. I. O'DRISCOLL, *J. Polym. Sci. Polym. Chem.* 14 (1976) 883.
- 54. J. JACOB, L. H. L. CHIA and F. Y. C. BOEY, unpublished work.
- 55. A.K. BOSE, M. S. MANHAS, M. GOSH, V. S. RAJU, K. TABEI and Z. URBANCZYK-LIPKOWSKA, *Heterocycles* 30(2) (1990) 741.
- 56. F. M. THULLIER, H. JULLIEN and M. F. GREMIER-ROUSTALOT, *Polym. Commun.* 27 (1986) 206.
- 57. N. BELDJOUDI, A. BOUAZIZI, D. DOUBI and A. GOUR-DENE, *Eur. Polym. J.* 24 (1988) 49.
- 58. N. BELDJOUDI and A. GOURDENE, *Ibid.* 24 (1988) 53.
- 59. *Idem., ibid.* 24 (1988) 265.
- 60. J.T.M. LINDERS, J. P. KOKJE, M. OVERHAND, T. S. LI E and L. M AAT, *Recl. Tray. Chim. Parp-Bas* 107 (1988) 449.
- 61. A.B. ALLOUM, B. LABIAD and D. VILLEMIN, *J. Chem. Soc. Chem. Commun.* (1989) 386.
- 62. G. ROUSSY, J. M. THIEBAUT, M. ANZARMOU, C. RICHARD and R. MARTIN, *J. Microwave Power Electromag. Energy, Syrup. Summ.* (1987) 169.
- 63. J.M. THIEBAUT, G. ROUSSY, G. MAIRE and E. GARIN, in International Conference on High Frequency Microwave processing and heating, Arnhem, Netherlands, 1989.
- 64. E. KARMAZSIN, P. SATRA and J. F. ROCHAS, *Thermochimica Acta* 93 (1985) 305.
- 65. E. KARMAZSIN, P. SATRA and P. BARHOUMI, *Thermochimica Acta Proc. ESTAC* (1984) 3.
- 66. S. M. SINGER, J. JOW, J. D. DELONG and M. C. HAW-LEY, *SAMPE Q* 20 (1989) 4.
- 67. J. WEI, J. JOW, J. DELONG and M. C. HAWLEY, *SAMPE* J. 27 (1991) 33.
- 68. F.Y.C. BOEY and C. Y. YUE, *J. Mater. Sci. Lett.* 10 (1991) 1333.
- 69. *F.Y.C. BOEYandT. H. LEE,Rad. Phys. Chem. 38(1991)419.*
- 70. R.K. AGRAWAL and L. T. DRZAL *J. Adhesion* 29 (1989) 63
- 71. C.E. HOLCOMBEandN. L. *DYKES,J. Mater. Sci. 26(1991)* 3730.
- 72. K. CHATAKONDU, M. L. H. GREEN, D. M. P. MINGOS and S. M. REYNOLDS, *J. Chem. Soc. Chem. Commun.* (1989) 1799.
- 73. D. R. HWANG, S. MOERLEIN, L. LANG and M. J. WELCH, *Ibid.* (1987) 1799.

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