RESEARCH ARTICLE

The Free-Radical Copolymerization of Difurylmethane with Maleic anhydride

Wilfred A. A. Ddamba,* Jane C. Ngila, Thabo T. Mokoena and Katherine Motlhagodi

Department of Chemistry, University of Botswana, Private Bag 0022, Gaborone, Botswana

*To whom correspondence should be addressed; e-mail: ddambawa@mopipi.ub.bw

Abstract

The copolymerization of difurylmethane with maleic anhydride in the presence of azobisisobutyronitrile as an initiator has been investigated at 65 °C, 72 °C and 85 °C in different solvents. Reaction feeds containing 85 mol % and higher of difurylmethane yielded a soluble alternating copolymer in which the furan residue entrained in the polymer chain formed 2,5 linkages and had 3,4 unsaturation. The 1:1 difurylmethane–maleic anhydride adduct was readily prepared, and at the above temperatures and in the presence of the radical initiator partially underwent retro-Diels–Alder reaction. Copolymerization of the difurylmethane and maleic anhydride thus formed yielded the unsaturated alternating copolymer. Copolymers prepared from reaction feeds with proportions of difurylmethane lower than 85 mol % had higher cross-link density and exhibited higher thermodecomposition temperatures.

Keywords: difurylmethane; maleic anhydride; copolymerization; thermodecomposition

1. Introduction

The free radical copolymerization of furan (F) and 2-methylfuran with maleic anhydride (MAH) has been extensively studied.[1,2,3] Kuramoto *et al.*[4] have also

reported an alternative thioglycolic acid-initiated method for this copolymerization at 25 °C. For both synthetic routes, ^{1}H-NMR and IR spectroscopic studies established the formation of an equimolar unsaturated F–MAH alternating copolymer in which the furan residue in the polymer backbone formed 2,5 linkages and contained 3,4 unsaturation.

With furan the least aromatic, and therefore the most pronouncedly dienic, of the five-membered aromatic heterocycles, its tendency to participate in Diels–Alder (DA) cycloaddition reactions as a diene has been studied extensively.[7] Recently Gandini *et al.*[8,9,10] have used bisdienophiles in DA reactions to crosslink polymer chains containing furanic moieties and have assessed the relative thermal stability of the resulting products. Spectroscopic evidence supported by TGA measurements indicated the presence of adduct structures that are formed between the bisdienophiles and the furan moieties and that are stable at temperatures up to 350 °C.[9] As would be expected on steric grounds, it was also demonstrated that pendant furan rings joined to the polymer backbone through the C-2 position are most reactive to cycloaddition.

In this paper we describe studies of the free radical copolymerization of MAH with difurylmethane (DFM), a dimer that forms in considerable proportions during the preparation of furfuryl alcohol resin.[5,6] In order to facilitate the understanding and the interpretation of the spectroscopic fine structure of the DFM–MAH copolymer produced, we prepared and characterized the 1:1 and 1:2 DFM–MAH DA adducts. The thermal stability of polymers prepared from reaction feeds of different compositions of DFM and MAH has been investigated by thermal analysis.

2. Experimental

Analytical grade MAH (UniLab, S.A.) was purified by sublimation of the commercial product. Acetone, ethyl acetate, dioxane and benzene (Aldrich Chemicals) were purified and dried in the usual manner. Analytical grade THF (Merck–Schuchardt) was used without further purification. Azobis(isobutyronitrile) (AIBN) (Aldrich Chemicals) was recrystallized three times from ethanol and dried under partial vacuum.

Measurements

^{1}H-NMR spectra were recorded in DMSO-d_6 on a Bruker AMX-300 MHz spectrometer at room temperature, and FT-IR (KBr pellets) spectra were recorded on a Perkin-Elmer 2000 FT spectrometer. Number average and weight average

molecular weights (M_n and M_w) and molecular weight distributions (M_w/M_n) of the polymers were determined by gel permeation chromatography (GPC) on the basis of STK polystyrene calibration standards (lot nos. TS-203, TS-204, TS-501 and TS-503 with M_n values of 9.1×10^3, 4.18×10^2, 1.05×10^3 and 5.97×10^3 respectively; Tosoh Corporation, Japan). The GPC system consisted of a Waters model M510 solvent delivery apparatus set at 500 psi for a flow rate of 1 cm^3 min^{-1}; a Waters model U6K injector, and a Waters model M401 differential refractometer detector. Two ultrastyragel GPC columns (both Waters, 7.8×300 mm: one HR1 part no. WAT044234 and the other HR2 part no. WAT044237) were connected to the chromatographic system and calibrated at ambient temperature. The THF mobile phase was filtered with a Waters 0.45 μM filter and degassed under partial vacuum. Thermogravimetric analyses were performed on a SDT 2960 – DTA-TGA Thermal Analyzer (TA Instruments) using 5 to 10 mg samples in Pt pans in a nitrogen atmosphere at a heating rate of up to 10 ºC min^{-1}. Degradation temperatures were determined at the temperature corresponding to a 5% weight loss.

***Preparation of the 1:1 and 1:2 DFM–MAH Diels–Alder Adducts***

The DFM used in this study was prepared as described elsewhere,[11] and its purity confirmed by elemental analysis. The two compounds, with DFM in tenfold molar excess, were dissolved in dioxane and the solution was allowed to stand for 24 h at room temperature. The 1:1 DFM–MAH Diels–Alder adduct formed was precipitated in *n*-hexane and washed with several further portions of *n*-hexane. The exclusively *exo*-adduct formed (m.p. 114 ºC) was dried under partial vacuum at room temperature. Its structure and stereochemistry were confirmed using ^{1}H-NMR (see results and discussion). The 1:2 DFM–MAH adduct (m.p. 116 ºC by DSC) was similarly prepared but in the presence of an excess of MAH, and was poorly soluble. The elemental analyses of the adducts were found to be as follows:

1:1 DFM–MAH adduct. Found: C, 63.03; H, 4.24; O, 32.73. Calcd. for $C_{13}H_{10}O_5$: C, 63.42; H, 4.09; O, 32.49%.

1:2 DFM–MAH adduct. Found: C, 60.24; H, 3.60; O, 36.16. Calcd. for $C_{17}H_{12}O_8$: C, 59.31; H, 3.51; O, 37.18%

Preparation of the Copolymers

Copolymerization reactions were carried out in benzene, acetone or ethyl acetate. Solutions of DFM and the AIBN initiator (0.1 mol % or less) were mixed and added in a single portion to a preheated solution of MAH at the appropriate reaction temperature. All reactions were carried out in a nitrogen atmosphere for durations up to 24 h. Scheme 1 summarizes the synthetic approach adopted in this study for the preparation of the DFM–MAH alternating copolymer using either the DFM and MAH co-monomers, or the 1:1 DFM–MAH Diels–Alder adduct.
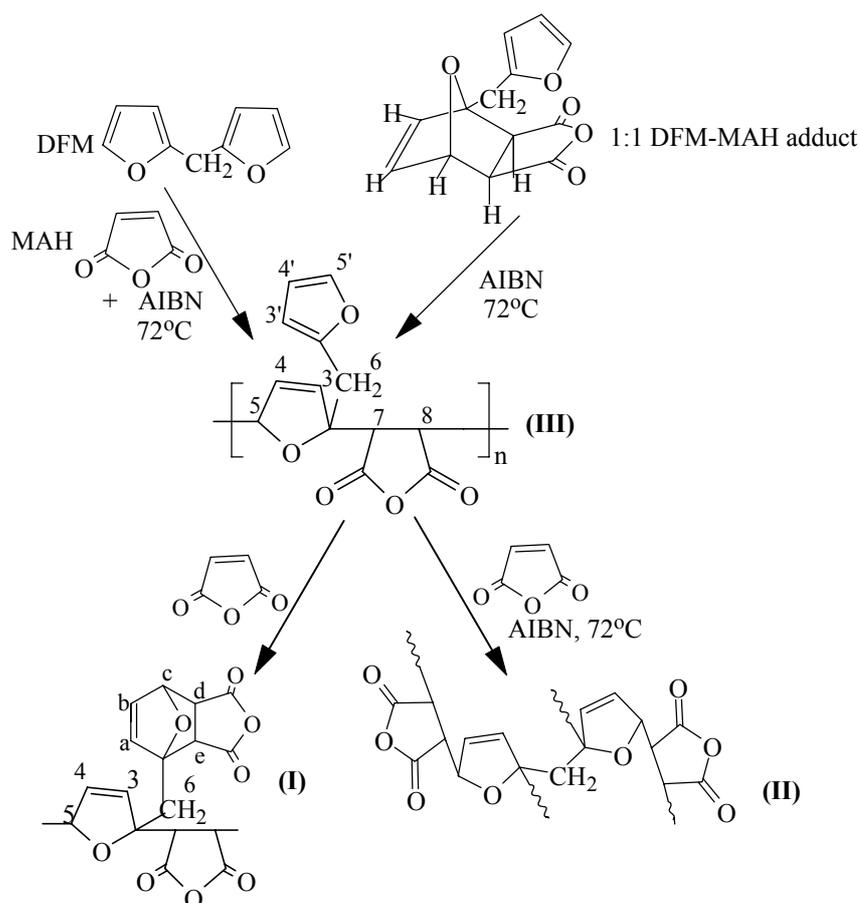
Scheme 1   Synthesis of DFM–MAH copolymers.

Copolymers prepared from reaction feeds in which the proportion of MAH was 15 mol % and above readily precipitated in the first 30 min. Precipitation took longer for reaction mixtures with lower MAH proportions. The unreacted MAH was removed by Diels–Alder cycloaddition with an excess of furan. The polymeric product was Soxhlet-extracted with benzene for at least 8 h and thereafter dried in a nitrogen atmosphere at 50 ºC to constant weight. Polymers prepared at 65 ºC were yellowish-

white, whereas at 72 ºC and above they were cream-white. The 1:1 DFM–MAH adduct was polymerized in acetone by adding the initiator to a nitrogen-purged and preheated adduct solution at 65 ºC. The polymer was thereafter purified as described above. Table 1 summarizes the polymer preparation conditions and the yields and the molecular weights of the polymers produced.

Table 1   Copolymerization of difurylmethane (DFM) and maleic anhydride (MAH).

Copolymer Sample Number	DFM : MAH mole ratio in reaction feed	Reaction Temp. (ºC)	Yield (%)	M_n; M_w/M_n
P$_1$	20 : 1	72	35.6	3169; 1.22
P$_2$	10 : 1	72	37.4	3640; 1.35
P$_{3(i)}$	5 : 1	72	48.5	3830; 1.54
P$_{3(ii)}$	5 : 1	84	57.8	3740; 1.61
P$_{3(iii)}$	5 : 1	65	40.7	3980; 1.43
P$_4$	3 : 1	72	62.4	—
P$_5$	1 : 2	72	64.2	—
P$_{(Adduct)}$	1 : 1	72	38.4	3920; 1.14

Elemental analyses (%) of the polymers yielded the following results: **P$_1$**: C, 62.73; H, 3.84; O, 33.43. **P$_2$**: C, 62.81; H, 3.91; O, 33.28. **P$_{3(i)}$**: C, 62.94; H, 4.04; O, 33.02. **P$_{3(ii)}$**: C, 62.96; H, 3.96; O, 33.08. **P$_{3(iii)}$**: C, 62.84; H, 3.82; O, 33.34. **P$_4$**: C, 62.43; H, 4.12; O, 33.45. **P$_5$**: C, 62.58; H, 3.69; O, 33.73. **P$_{adduct}$**: C, 62.74; H, 3.73; O, 33.49. The calculated value for the repeat unit **III** (Scheme 1) of a high molecular weight product is C, 63.42; H, 4.09; O, 32.49%.

3.   Results and Discussion

Our investigations indicated that reaction feeds containing at least a fivefold molar excess of DFM over MAH yielded DFM–MAH copolymers that were soluble in polar solvents. Lower concentrations of DFM resulted in the formation of insoluble (partially cross-linked) products. Early precipitation of the products caused difficulty in keeping the reaction mixtures homogeneous throughout the polymerization process.

To the best of our knowledge, the 1:1 and the 1:2 DFM-MAH Diels-Alder adducts prepared in these studies have never been reported. Their formation was quantitative (80-86% yield) and the efficiencies of the method of their preparation were assessed by elemental analysis which indicated virtually 100% Diels-Alder coupling between DFM and MAH (see experimental section). In contrast, the percentage oxygen content and the percentage carbon content of the polymers (see experimental section) were, respectively, higher and lower than the expected values (C, 63.42; H, 4.09; O, 32.49) calculated for the repeat unit **III** (Scheme 1) of a high molecular weight product, assuming an infinite degree of polymerization. This difference was attributed to the formation of DA adduct moieties between the pendant furan rings and trace amounts of unreacted MAH.

3.1. FTIR Spectroscopy

The IR spectra of DFM and the two adducts (Figures 1A, 1B and 1C) facilitated the interpretation of the copolymer's spectral features.
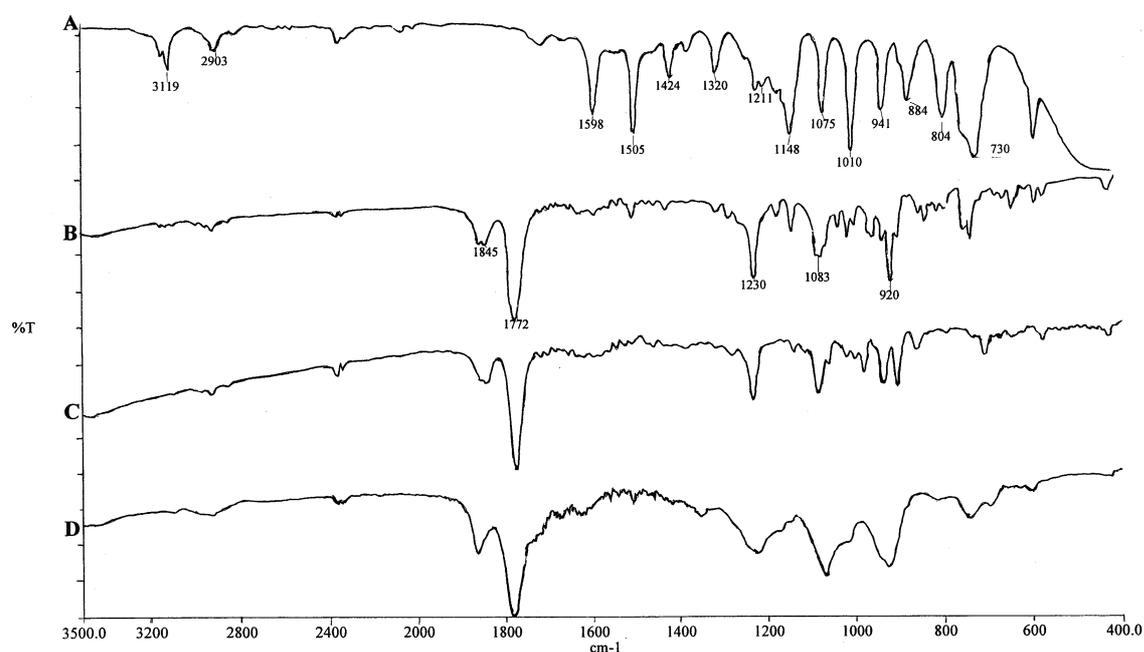
Figure 1 FTIR spectra (KBr pellets) of DFM (A), the 1:1 DFM–MAH DA adduct (B), the 1:2 DA adduct (C) and the DFM–MAH copolymer (D).

Figure 1D shows a typical copolymer FTIR spectrum (KBr pellets) for which the following band assignments (cm^{-1}) were made: 3119 (olefin and furan =C–-H); 2917 (aliphatic C–H); 1861 and 1783 (C=O); 1674 (C=C, furanic residue); 1610 and 1498 (C=C, furan ring); 1426 and 1348 (CH_2, rock); 1233 (C–O–C, furanic residue); 1147

(C–O–C, furan ring); 1080 (OC–O–CO, MAH residue); 925 (=C–H, breathing modes in furanic residue); 813, 741 and 693 (out-of-plane =C–H$_\alpha$, bending modes in the furan ring). The peaks around 2300 cm^{-1} are due to CO_2 in air and should be ignored. The polymerization reaction caused the intensity of the band at 925 cm^{-1} (olefin =C–H breathing modes in the furanic residue) to increase relative to the intensity of the band at 730 cm^{-1} (out-of-plane =C–H bending modes at the α-position of the furan ring). This implied that the addition polymerization process resulted in the furanic residue forming a 2,5-linkage with C_3=C_4 unsaturation as depicted in Scheme 1. The residual bands at 730 cm^{-1} persisted in the spectra of cross-linked products, suggesting a significant presence of unreacted furan rings in the insoluble product. The IR spectra of polymers prepared from different reaction feed mixtures showed no distinctive features characteristic of a specific method of preparation.

3.2. ^{1}H-NMR Spectroscopy

While the 1:1 DFM–MAH adduct was readily soluble in polar solvents such as acetone, the 1:2 adduct was only sparingly so, and solution ^{1}H-NMR analysis was therefore performed only on the 1:1 adduct. Figure 2 represents the ^{1}H-NMR of this adduct with peak assignments.

The protons of the CH$_2$ group are non-equivalent, and give rise to a four line AB system spectrum with a coupling constant of 15.7 Hz, and resonance peaks at δ 3.58 and 3.29 ppm. The two doublets centred at δ 3.56 and 3.42 ppm ($^3J_{H,H}$ = 6.72 Hz) were assigned to the non-equivalent protons H$_d$ and H$_e$, respectively, of the maleic anhydride residue.

Figure 3 shows a typical ^{1}H spectrum of the acetone-soluble DFM–MAH alternating copolymer.

By comparison with Figure 2, we assigned the peaks at δ 7.50 and 6.18 ppm respectively to the protons in the α and β positions of the furan rings pendant to the main polymer chain. The peak resonating at about 6.35 ppm arises from the olefinic *cis*-protons in positions 3 and 4 in the copolymer repeat unit (Scheme 1), while that at 5.44 ppm was assigned to the proton at position 5 of the furanic residue entrained in the main chain. The area of the peak envelope in the shift range 5.90–6.70 ppm relative to that at 7.50 ppm was at least 7:1, a ratio that was significantly greater than the expected value of 4:1.

7
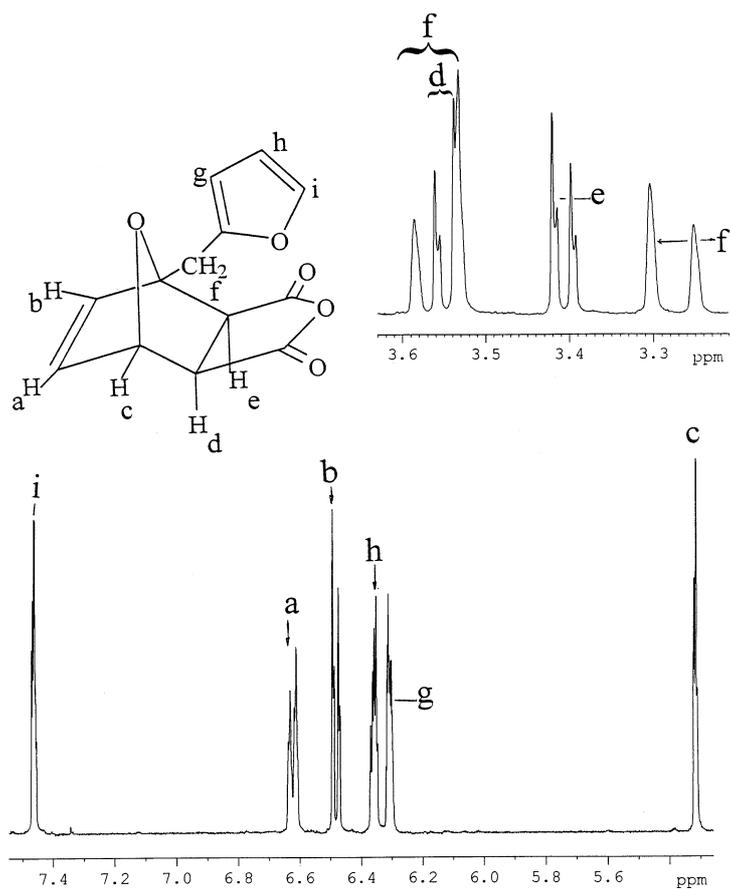
**Figure 2** ^{1}H-NMR spectrum of the 1:1 DFM–MAH, DA adduct in DMSO-d$_6$.
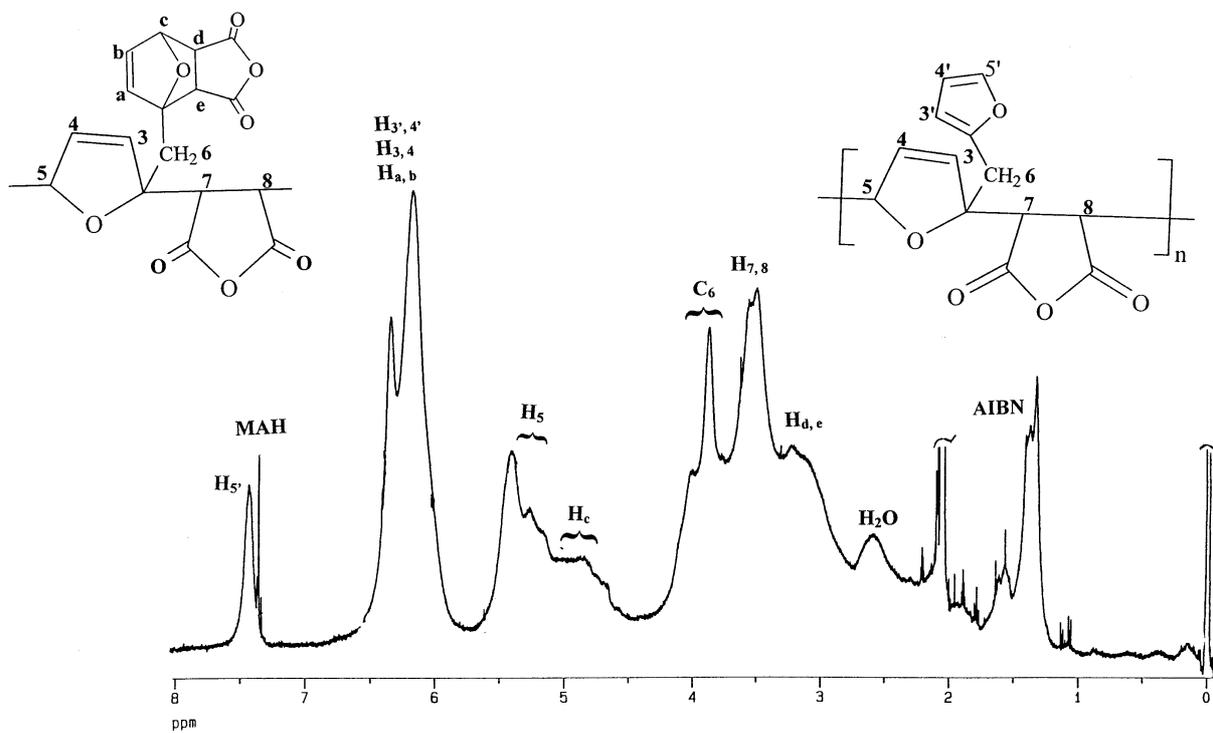
Figure 3 ^{1}H-NMR spectrum of the DFM-MAH copolymer in DMSO-d$_6$.

8

We attributed this increase in ratio to the formation of the DA adduct moieties between unreacted MAH and the furan rings pendant to the main polymer chain. The peak area in the shift range 5.90–6.70 ppm was thus enhanced by a contribution from the resonances due to H_a and H_b protons in the randomly distributed pendant adduct moieties in the unit such as **I**, (Scheme 1) along the polymer backbone. Similarly, the signal in the 4.50–5.20 ppm region was assigned to the proton H_c in the adduct unit **I**. The resonance band between 3.80 and 4.20 ppm consists of several overlapping peaks, and was assigned to the methylene protons of the pendant furfuryl groups. The well-developed peak centred at 3.54 ppm originates from the protons in positions 7 and 8 of the MAH residue in the chain, and is in the same resonance range as similar protons in the repeat units of the F–MAH and the cyclopentadiene–MAH copolymers.[2] We therefore suggest that the resonances appearing in the 2.70–3.40 ppm range be attributed to protons H_d and H_e in the possible *exo* and *endo* isomers of the pendant DA adduct groups, **I** in the polymer chain.

3.3. Thermal Stability

All the polymers exhibited a reproducible two-step thermal decomposition process accompanied by substantial weight loss in the temperature range of 290–440 °C. Figure 4 is a typical TGA–DTA traces for the DFM–MAH polymer.
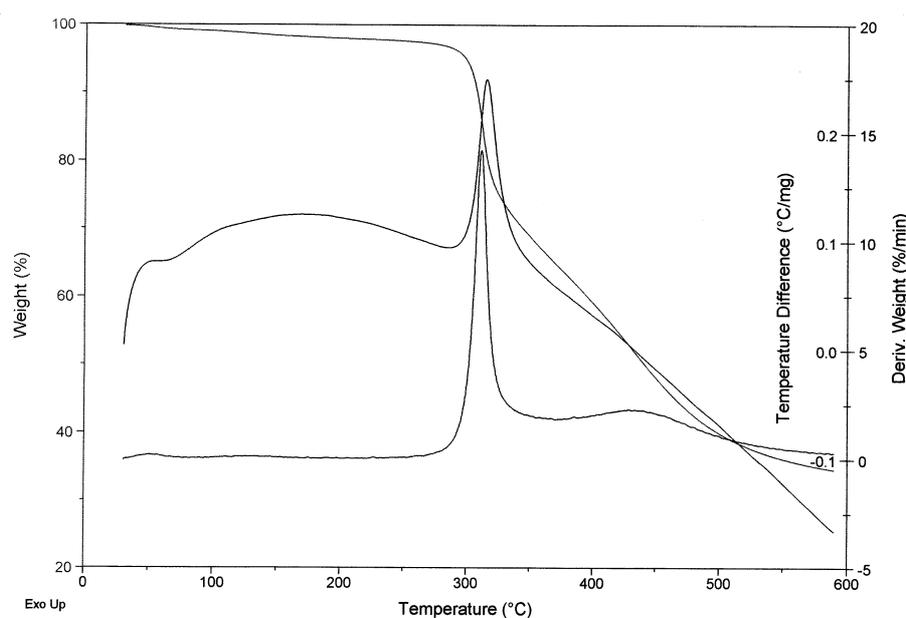
Figure 4 TGA–DTA tracings (10 min^{-1}, under nitrogen) of the DFM–MAH copolymer.

The small peak at 55 °C in the DTA trace was associated with the loss of surface moisture. The main exothermic thermal decomposition event, seen as a large peak in the DTA curve, occurred in the temperature range 290–325 °C and was accompanied by a weight loss of 30 to 34% for the different copolymers. Each polymer preparation had a unique decomposition temperature that increased with the proportion of MAH in the initial reaction feed (Table 2). We associated this apparent increase in thermal stability of the polymers with an increase in the degree of cross-link density. The broad second DTA peak occurred at about 435 °C for all the polymers with a weight loss of 22–26%. On thermal decomposition, polymers containing furan moieties form a high proportion of carbonaceous residue.[12] The linear DFM–MAH copolymers (**P₁**, **P₂** and **P₃**) contain a higher proportion of pendant furan rings than the insoluble products (**P₄** and **P₅**). As expected, we observed that the thermal decomposition of the soluble linear copolymers led to the formation of a higher proportion of carbonaceous residue (Table 2) than in the case of the insoluble products. The decreased proportion of carbonaceous residue for the latter suggested a decrease in furan moieties as a consequence of the partial cross-linking process. By comparison and in confirmation of this hypothesis, the exclusively straight-chain F–MAH copolymer with no pendant furan rings[4] exhibited the lowest decomposition temperature of 275 °C and formed the least carbon residue.
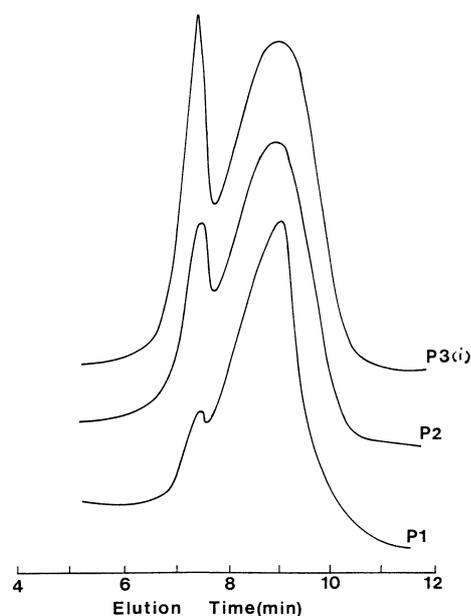
Table 2 Effect of the reaction feed composition on main DTA peak temperature, and the weight percent of carbonaceous residue.

Polymer	Reaction Feed mole ratio (DFM : MAH)	Main DTA Peak Temperature (°C)	% Carbonaceous Residue (600 °C)
P₁	20 : 1	294	40.9
P₂	10 : 1	297	39.3
P₃	5 :1	308	36.9
P₄	3 : 1	311	34.9
P₅	2 : 1	324	33.3
P (Adduct)	—	319	33.4
F–MAH*	1 : 1	275	27.0

* Included for comparison

3.4. Molecular Weights

The low molecular weights (Table 1) that were obtained for all soluble copolymers prepared in this study are attributed to the early precipitation of the products during the polymerization process. An additional contributory factor is the chain stiffness associated with the alternating sequences of the furanic and MAH residues in the main chain. Further purification of MAH and DFM through several cycles of sublimation and fractional distillation resulted in no observable increase in the measured molecular weights of the resulting copolymers. The GPC profiles of the polymers (Figure 5) indicated a bimodal molecular weight distribution for each sample, in which a small shoulder peak appeared on the high molecular weight side of the broad main peak. As the proportion of MAH in the reaction feed was increased, we observed an increase in both the intensity and the molecular weight attributable to the shoulder peak.

Figure 5 GPC chromatograms of soluble DFM–MAH copolymer preparations P_1, P_2 and $P_{3(i)}$. The initial reaction feed compositions for the polymers are indicated in Table 1.

Since TGA-DTA data had indicated that an increase in the thermal stability of the DFH-MAH copolymers with increased reaction feed proportion of MAH was attributable to an increase in the cross-link density, we therefore associated the increase in the intensity of the shoulder peak to an increase in the proportion of lightly cross-linked polymer chains in solutions of the soluble polymers.

4.   Conclusions

Our investigations showed that reaction feeds containing at least a fivefold molar excess of DFM over MAH yielded a soluble DFM–MAH copolymer. Lower DFM concentrations facilitated the formation of partially cross-linked products. DFM undergoes a free radical copolymerization with MAH to form unsaturated DFM–MAH copolymer as characterized by ^{1}H-NMR and FT–IR. The spectral characteristics of the DFM–MAH polymer exhibited less temperature-dependence than the F–MAH polymers. At 65 ºC a soluble copolymer with pendant furfuryl moieties is formed if the proportion of DFM in the reaction feed was at least 85 mol %. Lower DFM proportions and higher reaction temperatures promoted the formation of insoluble partially cross-linked products. The increase in the thermodecomposition temperature qualitatively indicated an increase of cross-link density in the products. The 1:1 DFM–MAH adduct undergoes a free radical polymerization reaction to form a soluble mixture of the unsaturated DFM–MAH alternating copolymer.

References

1   A.Gandini, *Adv. Polym. Sci.,* 1977, **25**, 47.

2   N. G. Gaylord, N. Martan and B. Achyut, *J. Polym. Sci., Polym. Chem. Ed.,* 1978, **16**, 1527.

3   A. Gandini, *Encyclopedia of Polymer Science and Engineering*, Wiley, New York, 1986, **7**, 454.

4   N. Kuramoto, K. Suda and K. Nagai, *J. Polym. Sci., Polym. Chem. Ed.,* 1989, **27**, 1713.

5   A. H. Fawcett and W. Ddamba, *Makromol. Chem.,* 1982, **183**, 2799.

6   A. H. Fawcett, T. F. Yau, J. N. Mulemwa and C. E. Tan, *British Polym. J.*, 1987, **19**, 211.

7   F. Fringuelli and A. Taticchi, *Dienes and Diels–Alder Reaction*, John Wiley, New York, 1990.

8   A. Gandini, C. Gousse and P. Hodge, *Macromolecules*, 1998, **31**, 314.

9   A. Gandini, and N. M. Belgacem, *Polym. Int*., 1998, **47**, 267.

10   A. Gandini and C. Gousse, *Polym. Int*., 1999, **48,** 723.

11   S. L. Buchwalter, *J. Polym. Sci., Polym. Chem. Ed.,* 1985, **23**, 287.

12   A. K. Sircar, *ACS Meeting, Rubber Division*, Ontario, Canada, May 1991.