

Thermally reversible highly cross-linked polymeric materials based on furan/maleimide Diels-Alder adducts

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Dedicated to Professor Antonino Corsaro on occasion of his seventieth birthday.

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ABSTRACT: A novel thermally reversible cross-linked polymer has been synthesized by a Diels-Alder (DA) reaction between bis(4-maleimido-phenyl)fluorene (cBMI) and tetrakis-furan monomers (4F) under microwave (MW) irradiation. The ultimate aim of this work was the preparation of a thermosetting material recyclable by a simple thermal treatment. The use of the MW irradiation was necessary because under thermal conditions the DA polymerization could lead to materials only partially cross-linked for a not desired equilibrium between DA and retro-DA processes induced by the high temperature. The easy thermal degradation of this cross-linked material was ascertained by appropriate experiments. Moreover, to better study the involved reactions of formation and decomposition, a more simple model-compound was also synthesized. The reported data confirm the recyclability of the synthesized cross-linked polymer by simply heating with the possibility of a regeneration of the polymer network by a further MW irradiation. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 42314.

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INTRODUCTION

In these last years, the synthesis of self-healing materials, characterized by the capability of self-repairing or recovering after mechanically or thermally induced damages, has become a new emerging and fascinating field of research.^{1–4} In this context, the Diels-Alder (DA) reaction constitutes a highly promising tool in order to introduce self-healing properties to polymeric systems.^{5–8} In fact, one of the most interesting characteristic of this reaction is the thermal reversibility of some DA adducts by which it is possible to regenerate the starting materials.

This intrinsic property suggests the synthesis of a new class of recyclable cross-linked polymers where the cross-link agent may be just the result of a DA multi-reaction.

Often, the DA reaction between furans and maleimide derivatives has been used for the formation of thermally reversible

bonds. This reversibility arises from the lower energy required to break the DA adducts with respect to any other covalent bond. Thus, after a DA reaction, the molecular structure can be subjected to dissociation upon heating, reforming the starting reagents (furan and maleimide derivatives) with the possibility, after cooling at room temperature, of the reconnection by application of a successive controlled heating.

This phenomenon is frequently used to “repair” the cracks occurring into polymeric materials. The reaction has been extensively developed and the suitability of a DA-system for self-healing of a bulk material (as linear polymers,⁹ networks,^{10,11} hydrogels,¹² and dendrimers¹³), adequately demonstrated.

The bis-maleimides based polymers are very interesting systems that possess many desirable properties such as a high tensile strength and an excellent chemical and corrosion resistance so

that they have been widely used as high-performance thermosetting resins.^{14,15} In particular, polymers containing fluorenyl structures in the back-bone, are generally indicated as *fluorenyl cardo* polymers. The presence of the *cardo* moieties can induce specific properties such as an excellent heat resistance and a good solubility.

In this manuscript we report the synthesis, based on a thermally reversible DA cycloaddition, of a cross-linked polymer system, starting from the reaction of bis(4-maleimido-phenyl)fluorene (cBMI) and a tetrakis-furan monomer (4F) under microwave (MW) irradiations (Scheme 1).^{16–19} The de-polymerization of the obtained polymer, by thermal treatment, was also verified. The ultimate aim of this work is the preparation of a thermosetting material that can be recycled by a simple thermal treatment. The use of the MW irradiation is linked to the consideration that under thermal conditions the DA polymerization could lead to materials only partially cross-linked due to a not desired equilibrium between DA and retro-DA processes induced by the high temperature.

A simpler molecular model based on *cardo* and furfuryl acetate was also synthesized and studied to better investigate the reversibility of the DA reaction.

All the synthesized products and their precursors were characterized by means of MALDI-TOF mass spectrometry, FT-IR, and NMR spectroscopy, and thermoanalytical techniques (TGA and DSC).

EXPERIMENTAL

Materials

All the solvents and basic materials were commercial products (Sigma-Aldrich) appropriately purified before use.

¹H-NMR Analyses

¹H-NMR, COSY, 2D NOESY, and ¹³C-NMR spectra were obtained on a UNITY^{INNOVA} Varian instruments operating at 500 or 200 MHz for ¹H and at 125 or 50 MHz for ¹³C using VNMR for software acquisition and processing. Samples were dissolved in CDCl₃ or DMSO-d₆ and the chemical shifts expressed in ppm by comparison with TMS or the solvents residue signal. The spectra were acquired at 27°C, with a spin lock time of 0.5 s. COSY and NOESY spectra were acquired using a Varian standard impulse sequence.

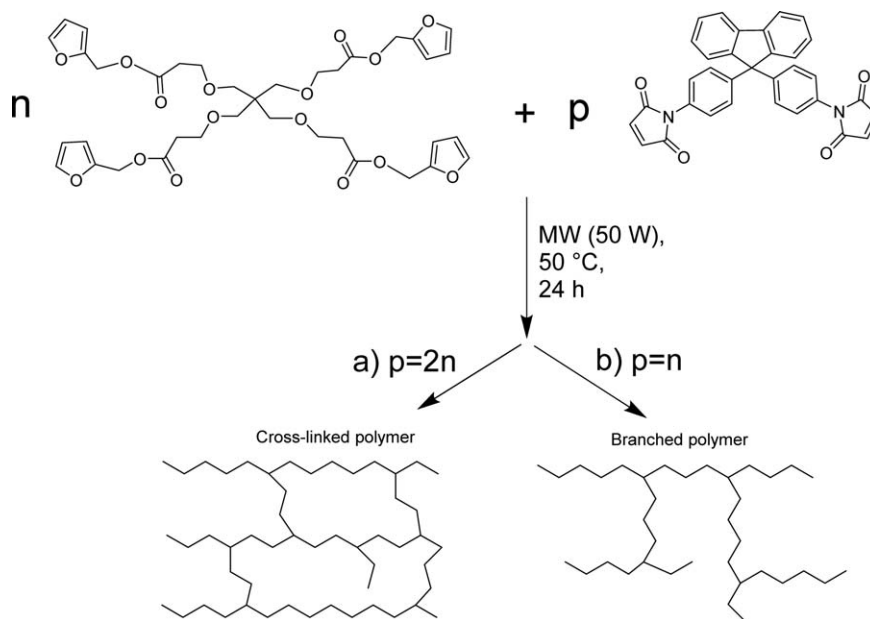
High resolution magic angle spinning (HR MAS) NMR spectra were recorded on a Bruker Avance spectrometer operating at 500 MHz proton frequency equipped with a dual ¹H HR-MAS probe head for semi-solid samples. Samples were transferred in a 4 mm ZrO₂ rotor containing a volume of about 50 μL. All the spectra were acquired with a spinning rate of 4 kHz to eliminate the dipolar contribution. The temperature was set and maintained at 300°K with an air flow of 535 L h⁻¹.

Microwave (MW) Irradiation

The reactions performed by microwave (MW) irradiation were conducted with a Microwave System apparatus (CEM Corporation). The samples, dissolved in CH₂Cl₂ in sealed tubes, were irradiated under microwave conditions at 50 W (2.45 GHz) and 50°C.

Thermal Analyses

Thermogravimetric (TGA) investigation was performed by means of a Perkin-Elmer Pyris TGA7, in the temperature range between 50 and 800°C (heating rate of 10°C min⁻¹), under nitrogen flow (60 mL min⁻¹). Differential scanning calorimetry (DSC) measurements were carried out by using a TA Q20 instrument equipped with a Refrigerant Cooling System (RCS) with a heating rate of 10°C min⁻¹, under an anhydrous N₂ atmosphere (60 mL min⁻¹).



Scheme 1. Synthesis of cBMI_{2n}-4F_n (a) and cBMI_n-4F_n (b).

MALDI-TOF MS Analyses

The MALDI-TOF mass spectra were collected by a Voyager DE (PerSeptive Biosystem) using a delay extraction procedure (25 kV applied after 2600 ns with a potential gradient of 454 V mm⁻¹ and a wire voltage of 25 V) with ion detection in linear mode.^{20,21} The instrument was equipped with a nitrogen laser (emission at 337 nm for 3 ns) and a flash AD converter (time base 2 ns). In order to avoid the polymer fragmentation, laser irradiance was maintained slightly above threshold. Each spectrum was an average of 32 laser shots. MALDI-TOF investigations were performed by loading on the sample plate 0.1 mmol of sample and 40 mmol of trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]-malonitrile (DCTB) as a matrix, using dimethylformamide (DMF) as solvent. 5,10-di(*p*-dodecanoxyphenyl)-15,20-di(*p*-hydroxyphenyl)porphyrin (C₆₈H₇₈N₄O₄, 1014 Da), tetrakis(*p*-dodecanoxyphenyl)porphyrin (C₉₂H₁₂₆N₄O₄, 1350 Da), and a polyethylene glycol (PEG) sample of known structure were used as external standards for *m/z* calibration.^{22–24}

FT-IR Analyses

FT-IR spectra were obtained as KBr disks by using a Perkin-Elmer Spectrum One spectrophotometer.

Determination of the Degree of Cross-Linking (DC)

The degree of cross-linking (DC) was determined using the Soxhlet extraction method.²⁵

Briefly, the specimen was crushed and the exact initial weight (*M*₁) was determined on a precision balance. The specimen was then put in a filter holder and refluxed for 8 h in CHCl₃.

After this treatment, the non-cross-linked fraction dissolved in the solvent was separated from the insoluble cross-linked material. This insoluble residue was dried at 80°C for 24 h and weighted (*M*₂). The DC was calculated as: DC = (*M*₂/*M*₁) * 100.

Synthesis of 9,9-Bis(4-maleimidophenyl)fluorene (cBMI)

To a well stirred solution of 6.86 g (0.07 mol) of maleic anhydride in acetic acid (120 mL), 8.7 g (0.025 mol) of 9,9-bis(4-aminophenyl)fluorene were slowly added over a period of 30 min at 0°C. After, the solution was stirred for 1 h and refluxed for additional 12 h. Then, the mixture was concentrated under reduced pressure and the residue purified by flash chromatography, using a mixture of cyclohexane/ethyl acetate 1 : 1 as eluent, to give cBMI (8.89 g, 70% yield) as a yellow solid.²⁶

¹H NMR [CDCl₃, 200 Mhz, Figure 1(a)] δ: 7.73 (d, 2H, H₁), 7.37–7.17 (m, 16H, H₂, H₃, H₄, H₅, and H₆), 6.79 (s, 4H, H₇).

¹³C NMR (50 MHz, DMSO-*d*₆) δ: 169.77 (C₁₂), 150.55 (C₆), 145.60 (C₈), 140.41 (C₁), 134.49 (C₁₃), 131.28 (C₁₁), 130.10 (C_{3,4}), 129.20 (C₉), 128.22 (C₁₀), 126.55 (C₅), 126.04 (C₅), 120.59 (C₂), 64.32 (C₇).

FT-IR (cm⁻¹), Figure 4: 3100 (—CH=CH—), 1770, 1707 (C=O), 1608 (C=C), 1150 (C—N—C of the maleimide). MALDI-TOF [Figure 2(a)]: *m/z* 509 (as MH⁺ species).

Synthesis of Tetrakis-Furan Monomer (4F)

This compound was prepared according to the method described by Wudl and coworkers,¹¹ starting from 6,6-bis(carboxy-2-oxabutyl)-4,8-dioxaundecane-1,11-dicarboxylic acid, thionyl chloride, and furfuryl alcohol. Briefly, 0.368 mL (4.5 mmol) of SOCl₂ were

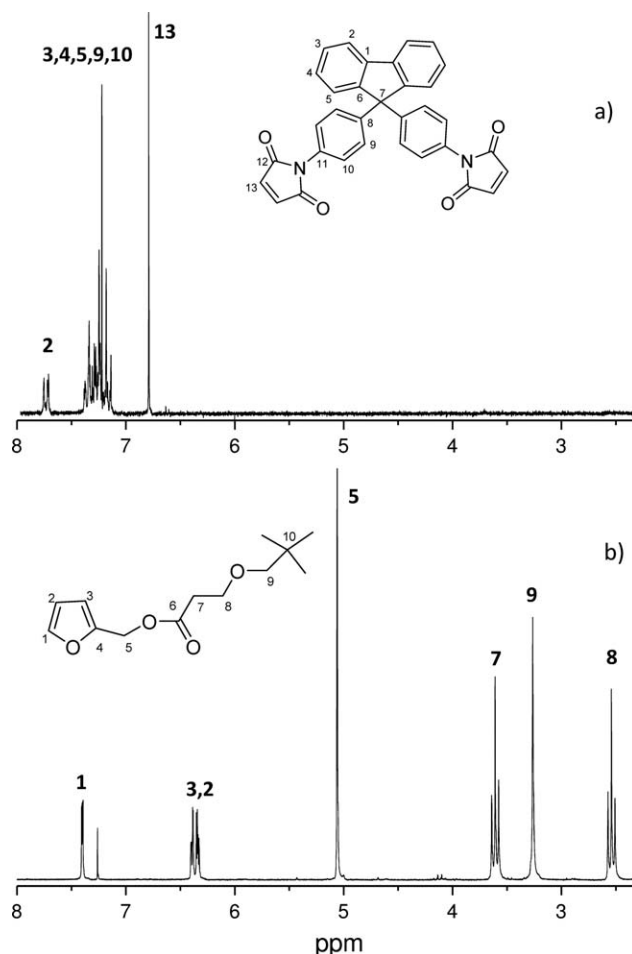


Figure 1. ¹H-NMR spectra (in CDCl₃) of cBMI (a) and 4F (b).

added to 104 mg (0.3 mmol) of 6,6-bis (carboxy-2-oxabutyl)-4,8-dioxaundecane-1,11-dicarboxylic solubilized in 4 mL of anhydrous CH₂Cl₂. The solution was refluxed overnight and successively evaporated under vacuum. The obtained product was solubilized in anhydrous THF then an excess of furfuryl alcohol and pyridine (2 mmol) were added. After 2 h the solution was filtered and evaporated under vacuum; the residue was then solubilized in CH₂Cl₂ and washed with water. The organic phase was dried with Na₂SO₄ and evaporated under vacuum. The obtained product was purified by mean of a chromatographic column packed with alumina, using ethyl acetate as eluent (83% yield).

¹H-NMR [CDCl₃, 200 MHz, Figure 1(b)], δ: 7.37–7.36 (m, 4H, H₁), 6.36–6.34 (m, 4H, H₂), 6.31–6.28 (m, 4H, H₃), 5.02 (s, 8H, H₅), 3.57 (t, *J* = 6.2 Hz, 8H, H₇), 3.23 (s, 8H, H₉), 2.50 (t, *J* = 6.2 Hz, 8H, H₈).

¹³C NMR (CDCl₃, 50 MHz), δ: 171.93 (C₉), 149.30 (C₈), 142.99 (C₁), 110.38 (C₃), 110.35 (C₂), 82.91 (C₇), 66.38 (C₆), 57.09 (C₄) 45.08, 34.71.

MALDI-TOF [see Figure 2(b)]: *m/z* 767 (as MNa⁺ species).

Synthesis of Model Compound (cBMI/Furfuryl Acetate)

A solution containing 0.056 g (0.40 mmol) of furfuryl acetate (2) and 0.0508 g (0.10 mmol) of cBMI in dry CH₂Cl₂ (2 mL)

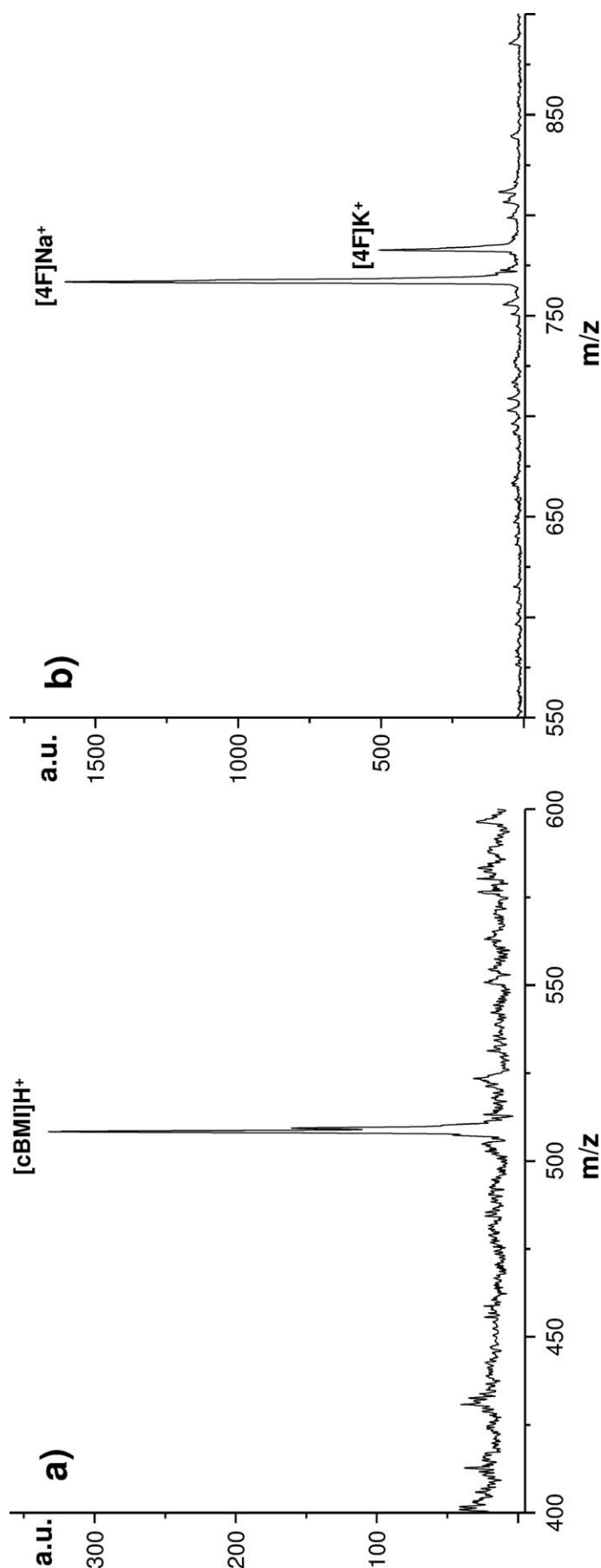


Figure 2. MALDI-TOF mass spectra of cBMI (a) and 4F (b).

was put in a sealed tube and irradiated under microwave conditions at 50 W and 50°C, for 30 min. The removal of the solvent in *vacuo* led to a crude material from which, after MPLC purification (using as eluent a mixture of cyclohexane/ethyl acetate 4:1) the adduct **3** and a mixture of **4** and **5** (Scheme 2) were obtained.

Chemical Characterization of: $\{(3aRS,4RS,7RS,7aSR)-2-[4-(9-\{4-[(3aRS,4SR,7SR,7aSR)-4-[(acetyloxy) methyl]-1,3-dioxo-3a,4,7,7a-tetrahydro-1H-4,7-epoxyisoindol-2(3H)-yl]phenyl\}9H-fluoren-9-yl)phenyl]-1,3-dioxo-2,3,3a,4,7,7a-hexahydro-1H-4,7-epoxyisoindol-4-yl)methylacetate$ (**3**)

This product was a light brown solid obtained with a yield of 56% whose structure was assigned by ¹H-NMR and NOESY spectra.

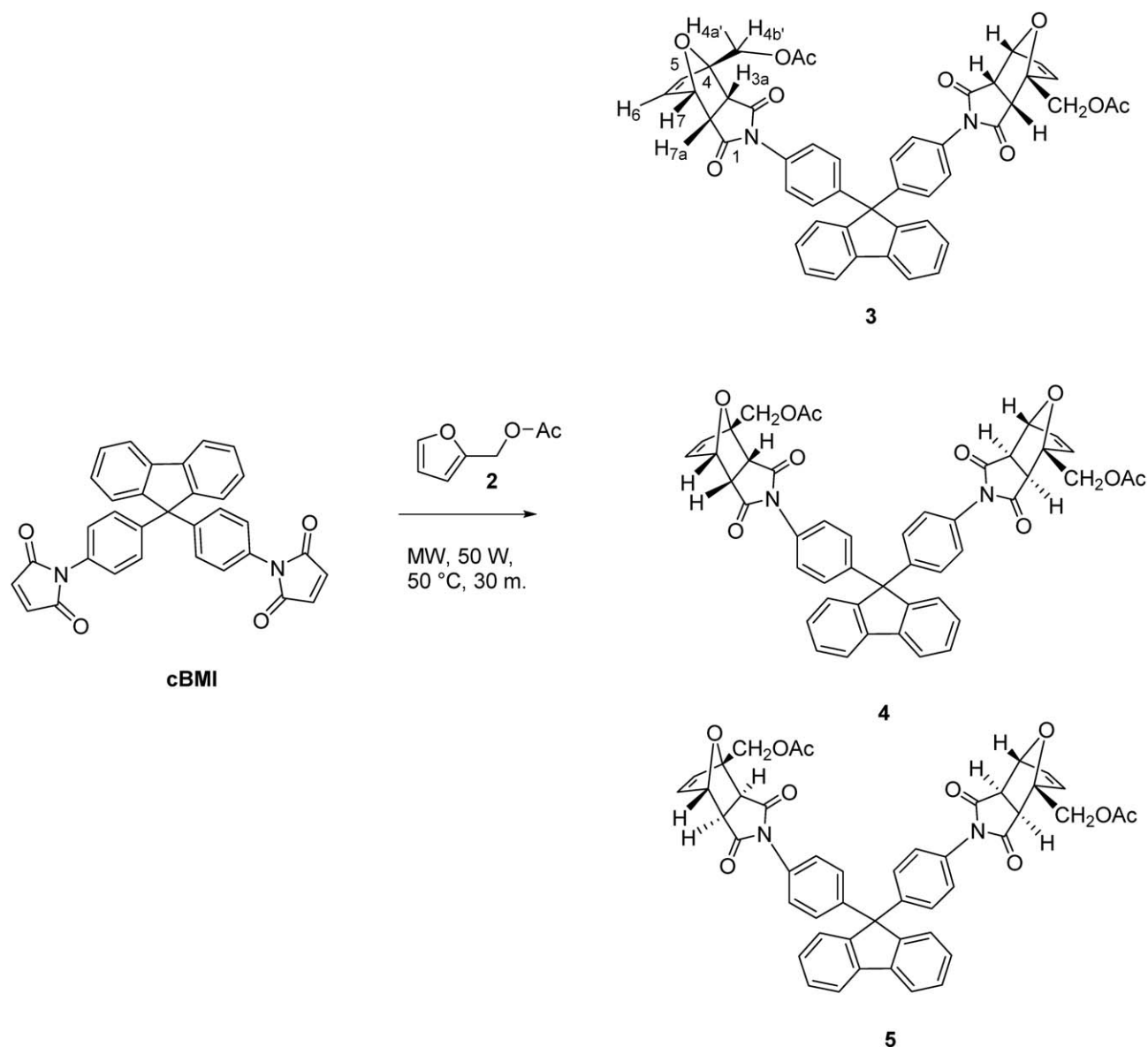
¹H NMR [500 MHz, CDCl₃, Figure 7(a)] δ : 7.76 (d, $J = 10.0$ Hz, 2H aromatic protons), 7.38 – 7.33 (m, 4H aromatic protons), 7.29–7.25 (m, 6H aromatic protons), 7.14 – 7.12 (m, 4H aromatic protons), 6.57 (dd, $J = 5.5$ and 1.5 Hz, H₆, 2H), 6.44 (d, $J = 5.5$ Hz, H₅, 2H), 5.35 (d, $J = 1.5$ Hz, H₇, 2H), 4.97 (d, $J = 15.0$ Hz, H_{4'a}, 2H), 4.45 (d, $J = 15.0$ Hz, H_{4'b}, 2H), 3.11 (d, $J = 5.0$ Hz, H_{7a}, 2H), 3.02 (d, $J = 5.0$ Hz, H_{3a}, 2H), 2.08 (s, 6H).

¹³C NMR (125 MHz, CDCl₃) δ : 174.67, 173.20, 170.35, 150.02, 146.09, 140.04, 137.58, 137.18, 130.12, 128.80, 127.91, 127.82, 126.19, 126.12, 120.23, 89.82, 81.44, 64.93, 61.32, 49.88, 48.32, 20.62. MALDI-TOF: m/z 789 (as MH⁺ species).

The relative configuration of **3** was assigned examining its NOESY spectra. In particular, a positive NOE effect was observed for H–6 (6.57 δ) and H–7a (3.11 δ), upon irradiation of H–7 at 5.35 ppm. Analogously, irradiation of H–6 resulted in an enhancement of the signals corresponding to H–5 (6.44 δ), H–7, and H–7a. Moreover, irradiation of H–5 induced a positive NOE effect for H–6, H–4'b (4.45 δ), and H–3a (3.02 δ) and a weak effect for H–4'a (4.97 δ). Finally, irradiation of H–3a gave rise to strong enhancements for H–7a and H–4'b, and a weak effect for H–4'a and H–5. This result is clearly indicative of their ENDO-ENDO relationship.

$\{(3aSR,4RS,7RS,7aRS)-2-[4-(9-[4-[(3aSR,4SR,7SR,7aRS)-4-[(acetyloxy)methyl]-1,3-dioxo-3a,4,7,7a-tetrahydro-1H-4,7-epoxyisoindol-2(3H)-yl]phenyl\}9H-fluoren-9-yl)phenyl]-1,3-dioxo-2,3,3a,4,7,7a-hexahydro-1H-4,7-epoxyisoindol-4-yl)methylacetate$ (**4**) and $\{(3aRS,4RS,7RS,7aSR)-2-[4-(9-[4-[(3aSR,4SR,7SR,7aRS)-4-[(acetyloxy)methyl]-1,3-dioxo-3a,4,7,7a-tetrahydro-1H-4,7-epoxyisoindol-2(3H)-yl]phenyl\}9H-fluoren-9-yl)phenyl]-1,3-dioxo-2,3,3a,4,7,7a-hexahydro-1H-4,7-epoxyisoindol-4-yl)methylacetate$ (**5**) mixture

The mixture of **4** and **5** was a light brown solid obtained with a yield of 20%. ¹H NMR (CDCl₃, 200 MHz): δ 7.77–7.73 (m, 2H+2H), 7.37–7.23 (m, 12H+12H), 7.16–7.12 (m, 2H+2H), 6.97–6.89 (m, 2H+2H), 6.62–6.41 (m, 2H+2H), 5.42–5.37 (m, 2H+2H), 5.04–4.86 (m, 2H+2H), 4.64–4.42 (m, 2H+2H), 3.83–3.77 (m, 1H+1H), 3.53 (d, $J = 8.0$ Hz, 1H+1H), 3.13 (d, $J = 8.0$ Hz, 1H+1H), 3.02 (d, $J = 6.0$ Hz, 1H+1H), 2.14 (6H), 2.12 (s, 6H). MALDI-TOF: m/z 789 (as MH⁺ species).



Scheme 2. Formation of 3-5 from reaction between **cBMI** and **2** by MW irradiation.

Retro Diels–Alder Reaction of Model Compounds 3–5

The mixture of 3–5 adducts (30 mg) was dissolved in DMSO- d_6 (0.6 mL) directly in a NMR tube and heated at 120°C. After 5 h the solution was quickly cooled at 0°C and its $^1\text{H-NMR}$ spectrum recorded. This spectrum showed the signals due the unbonded **cBMI** and furfuryl acetate **2** (about 90% yield).

Synthesis of **cBMI**_{2n}-**4F**_n Cross-Linked Polymer

A typical procedure was as follows: 74.4 mg (0.1 mmol) of monomer **4F** and 101.6 mg (0.2 mmol) of monomer **cBMI** were dissolved in 5 ml of CH_2Cl_2 and the solution, in a sealed tube, irradiated under microwave conditions 50 W and 50°C. Although a precipitate appeared after 4 h, the irradiation was continued until completely disappearance of the starting materials, occurring after about 24 h. The resulting suspension was filtered and the residue washed with refluxing CH_2Cl_2 and dried

under vacuum. The resulting cross-linked polymeric material (yield about 80%) was then analyzed by FT-IR, ^1H HR-MAS, TGA, and DSC techniques.

Synthesis of **cBMI**_n-**4F**_m Branched Polymer

A typical procedure was as follows: 74.4 mg (0.1 mmol) of monomer **4F** and 50.5 mg (0.1 mmol) of monomer **cBMI** were dissolved in 5 ml of CH_2Cl_2 and the solution, in a sealed tube, irradiated under microwave conditions, 50 W and 50°C for 24 h. The resulting product was precipitated in Et_2O , filtered and dried under vacuum. The soluble fraction of the resulting polymeric material was analyzed by $^1\text{H-NMR}$, MALDI-TOF, TGA, and DSC techniques.

$^1\text{H-NMR}$ [CDCl_3 , 200 MHz, Figure 6(a)], δ : 7.75 (d, H_2), 7.39–6.95 (br m, $\text{H}_{3,4,5,9,10}$), 6.82 (s, α), 6.59–6.25 (br m, $\text{H}_{16,15}$), 5.33

(br m, H_{14}), 5.08 (br s, H_{17}), 4.86–4.22 (br d, $H_{17a+17b}$), 3.59 (br m, H_{18}), 3.25 (br s, H_{20}), 2.52 (br m, H_{19}).

RESULTS AND DISCUSSION

To obtain the cross-linked polymer, the precursors **cBMI** and **4F** were prepared according to the methods described in the experimental section. In particular, **cBMI** was obtained with a procedure similar to that described by Kumar and coworkers,²⁶ starting from maleic anhydride and 9,9-bis(4-aminophenyl)fluorene. **4F** was obtained according to the method described by Wudl and coworkers,¹¹ starting from 6,6-bis(carboxy-2-oxabutyl)-4,8-dioxaundecane-1,11-dicarboxylic acid, thionyl chloride, and furfuryl alcohol.

Chemical structures of these products were confirmed by means of NMR spectroscopy (see Figure 1 and experimental section) and MALDI-TOF mass spectrometry (Figure 2). In particular, the mass spectrum of **cBMI**, reported in Figure 2(a), shows a signal at m/z 509 due to the corresponding molecular ion detected as MH^+ , while the mass spectrum of **4F**, Figure 2(b), consists essentially in its molecular ion peak at m/z 767 detected as MNa^+ with the presence of a less intense peak at m/z 783 due to the MK^+ species.

The cross-linked polymer was synthesized (see Scheme 1, route a) by means of DA reaction between **cBMI** and **4F** (molar ratio 2 : 1, **cBMI**_{2n}-**4F**_n) in CH_2Cl_2 solution, in a sealed tube and under MW irradiation (50W, 50°C; condition chosen after several experimental tests). The formed product resulted in a light-yellow insoluble material (90% yield). The solid state NMR spectrum (Figure 3) and inset of Figure 6, for signals assignment) of this cross-linked polymer shows signals compatible with the presence of the **cBMI/4F** adduct. In particular, the presence of signal at about 5.3 ppm, due to the protons H_{14} of 2,5-dihydrofuranyl system, and the lack of signal at 6.79 ppm (imide moiety) are diagnostic of the DA adduct formation.

As a further confirmation of the polymerization process, a series of FT-IR spectra were acquired. Figure 4 shows the spectra of **cBMI** (dashed line), **4F** (dotted line) and of the cross-linked

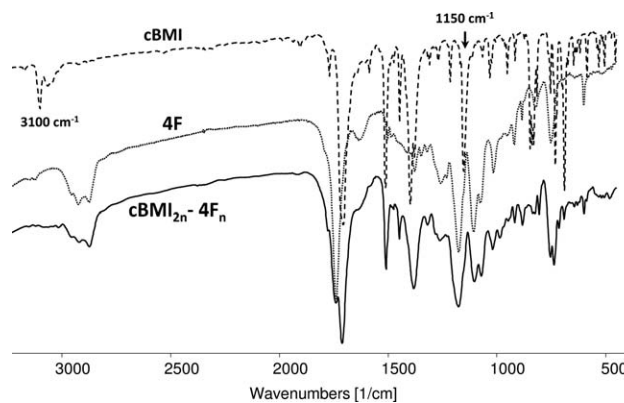


Figure 4. FT-IR spectra of **cBMI** (dashed line), **4F** (dotted line) and cross-linked polymer **cBMI**_{2n}-**4F**_n (continuous line).

polymer (continuous line). It is evident as, due to the cycloaddition reaction, the spectrum of the cross-linked polymer (Figure 3, continuous line) lacks the signal at about 3100 cm^{-1} ($-\text{CH}=\text{CH}-$) of the maleimide moiety,²⁶ instead present in **cBMI** spectrum (Figure 3, dashed line). On the base of the FT-IR spectrum of the cross-linked material [disappearance of the signals at 3100 cm^{-1} ($-\text{CH}=\text{CH}-$) and at 1150 cm^{-1} ($\text{C}-\text{N}-\text{C}$ of the maleimide²⁶)] and experiments of extraction with solvent (Soxhlet extraction method²⁵), a DC higher than 75% was estimated.

To a better understanding the polymeric structure obtained in the DA coupling, a new polymerization process was performed adopting a 1/1 **cBMI/4F** molar ratio (see Scheme 1, route b) to obtain a branched polymeric system. The reaction led to the formation of a partially soluble product, suitable to be analyzed by means of MALDI-TOF and ¹H-NMR techniques. As expected, the MALDI-TOF spectrum (Figure 5) of the soluble fraction of **cBMI**_n-**4F**_m shows peaks due to the formation of several DA adducts. In particular, there are evident peaks at m/z 1275, 1783, 2019, and 2527, assigned to the molecular species of **cBMI**₁-**4F**₁, **cBMI**₂-**4F**₁, **cBMI**₁-**4F**₂, **cBMI**₂-**4F**₂ (with the subscript numbers indicating the amount of units present in each species), respectively, all detected as adduct with Na^+ .

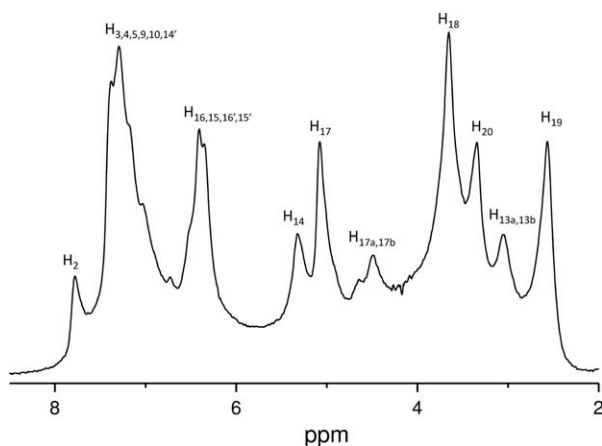


Figure 3. ¹H HR-MAS spectrum of cross-linked polymer **cBMI**_{2n}-**4F**_n (see inset Figure 6 for peaks assignment).

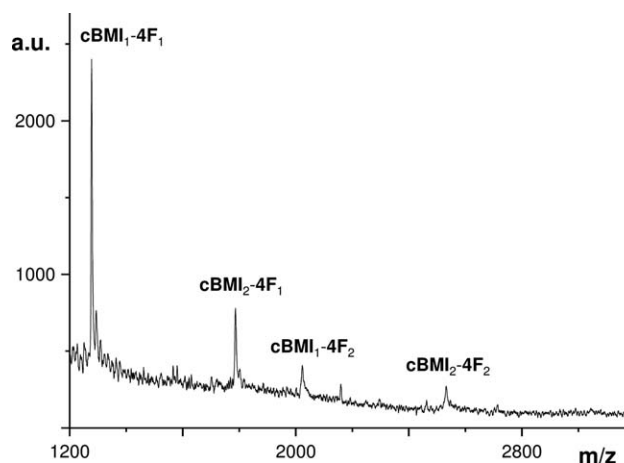


Figure 5. MALDI-TOF mass spectrum of **cBMI**_n-**4F**_m.

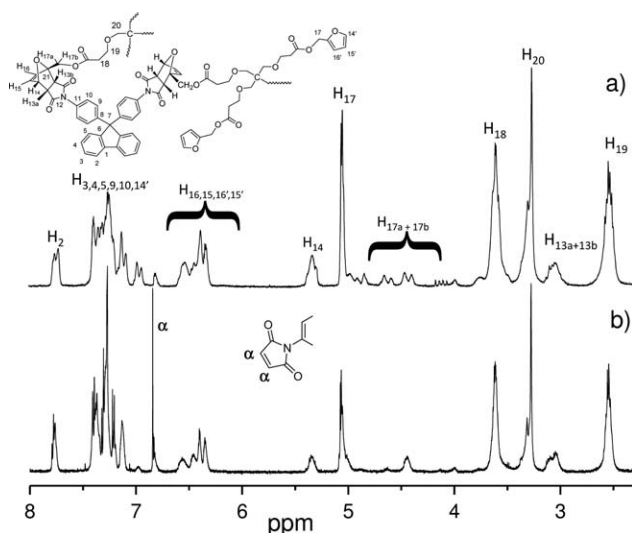


Figure 6. ¹H-NMR spectra (in CDCl₃) of soluble fraction of cBMI_n-4F_m branched polymer (a) and its thermal treatment (b).

The ¹H-NMR spectrum of soluble fraction of cBMI_n-4F_m branched polymer [Figure 6(a)] shows, as already seen in the ¹H HR-MAS spectrum (Figure 3), besides of the signal at 6.79 ppm due to imide functionality, the presence of the signal at about 5.25 ppm corresponding to the protons at H₁₄ of the 2,5-dihydrofuranly moiety, and the signals of the diastereotopic methylene protons at about 4.9 and 4.5 ppm (H_{4'a} and H_{4'b}) resonating as doublet of doublets due to the presence of the stereo-centre at carbon 21.

The retro-DA reaction of the cross-linked polymers (cBMI_{2n}-4F_n) was performed by heating, at 120°C for 20 min of its DMSO dispersion and successive quick cooling at 0°C. The total solubility in organic solvents of the obtained materials was strongly indicative of the occurrence of the de-polymerization reaction.

The same treatment was also conducted on the soluble fraction of cBMI_n-4F_m branched polymer, and the resulting product was analyzed by means of ¹H-NMR experiments [see Figure 6(b)]. The data confirm that, after heating, the intensity of the DA adducts signals (H₁₄, H_{17a}, H_{17b}, H_{13a}, and H_{13b}) decrease, while the signal at 6.79 ppm, of the cBMI imide function, increases.

On the bases of the maleimide residual signal, α, with respect to H₂ (see Figure 6), the degree of the retro-DA reaction was evaluated about 33%.

To prove the reversibility of the cross-linking phenomenon, the DA/retro-DA process was repeated four times on the same specimen (cBMI_{2n}-4F_n or cBMI_n-4F_m), obtaining always the reticulation, under MW condition, and the de-polymerization, after each heating process.

However, to further confirm the retro DA process, the same synthetic procedure was performed on a simpler molecular system, a bis-furfuryl acetate/cBMI adduct, obtained (see Scheme 2) from a mixture of furfuryl acetate (2) and cBMI in anhydrous CH₂Cl₂, placed in a sealed tube and irradiated under

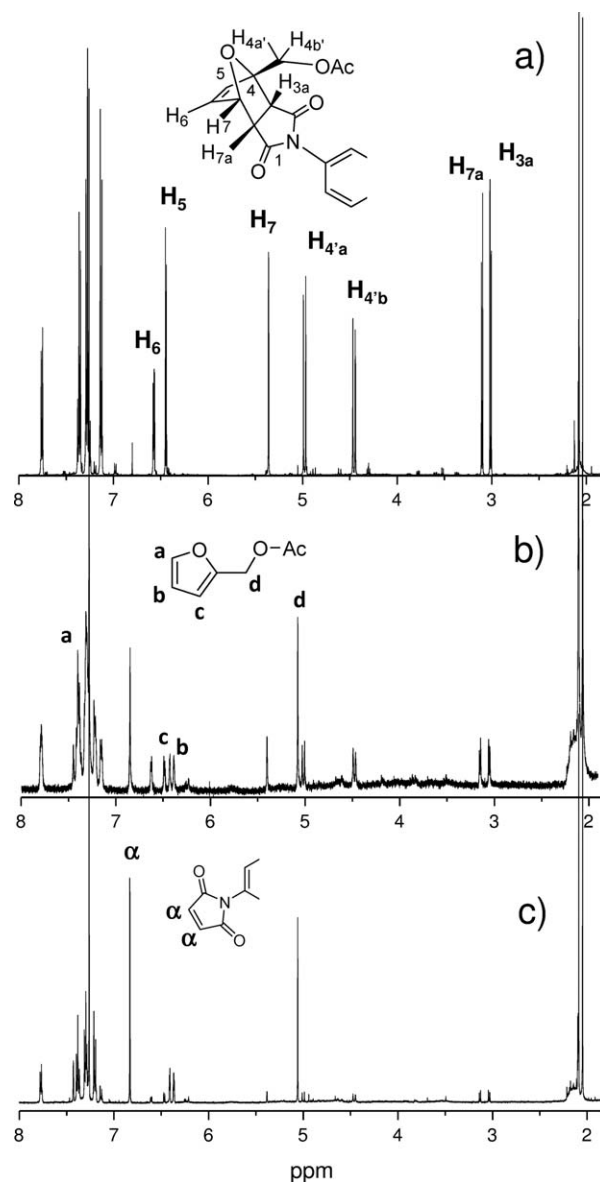


Figure 7. ¹H-NMR of 3 (a) and 3 after thermal treatment at 120°C for 1 h (b) and 5 h (c).

microwave (50 W, 50°C) for 30 min. After MPLC purification [using a mixture of cyclohexane/ethyl acetate (4 : 1) as eluent], adduct 3 and a not separable mixture of 4 and 5 were collected and characterized by ¹H-NMR analysis [in Figure 7(a), the ¹H-NMR of 3 is reported].

The regeneration of the starting compounds was made by heating at 70°C for 5 h (in sealed tube) the compound 3 and a successive quickly cooling at 0°C. As expected, the ¹H spectrum of the resulting material [Figure 7(c)] shows the presence of cBMI and furfuryl acetate 2. In particular, the comparison of the ¹H-NMR spectrum of 3 [Figure 7(a)] with the spectra of the sample obtained after heating at 1 h and 5 h [Figure 7(b,c)], shows the disappearance of the peaks at 3.02, 3.11, 4.45, and 4.97 ppm, attributed to the DA adducts, and the presence of the signal at 6.8 ppm (imide proton). These results are a clear

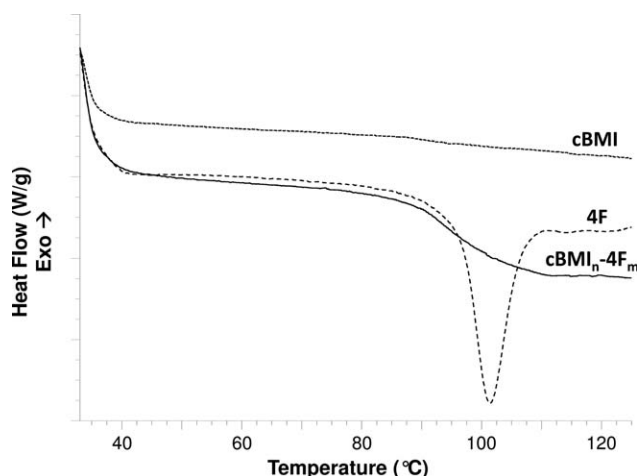


Figure 8. DSC traces of **cBMI** (dotted line), **4F** (dashed line) and **cBMI_n-4F_m** (continuous line).

evidence of the decomposition of **3** with formation of the starting materials.

To achieve further information on the thermal property of the monomers (**cBMI** and **4F**) and **cBMI_n-4F_m** branched polymer, DSC measurements were performed in the range 30–125°C. The obtained traces, Figure 8, show that **cBMI** does not exhibit any significant thermal process; on the contrary, **4F** shows a melting peak at 101.4°C. Instead, **cBMI_n-4F_m** branched polymer show a thermal transition at 97.5°C due to a glass transition phenomenon that is justified by the molecular mobility induced from the aliphatic **4F** segments present in the polymeric chains.

The thermogravimetric experiments, performed on **4F** in N₂ atmosphere (Figures 9 and 10, dashed line), reveal a fast one-step thermal-decomposition starting at about 270°C with a volatilization rate of about −11.8%/min, followed by a more slow process (−3%/min) at about 400°C, and the formation of a stable residue, at 800°C, of about 20%. Differently, **cBMI** (Figures 9 and 10, dotted lines) exhibits a slower degradation

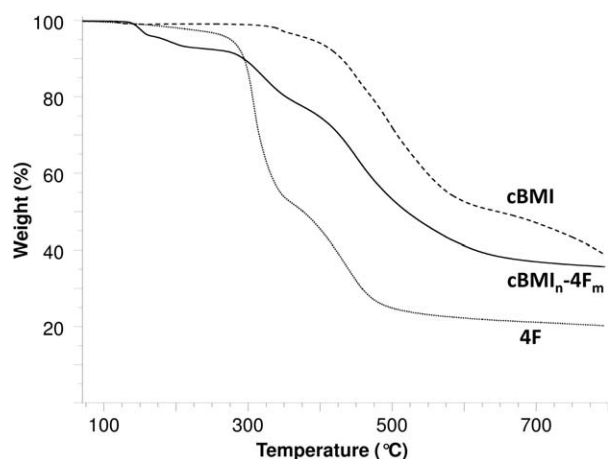


Figure 9. TGA traces of **cBMI** (dashed line), **4F** (dotted line) and **cBMI_n-4F_m** (continuous line).

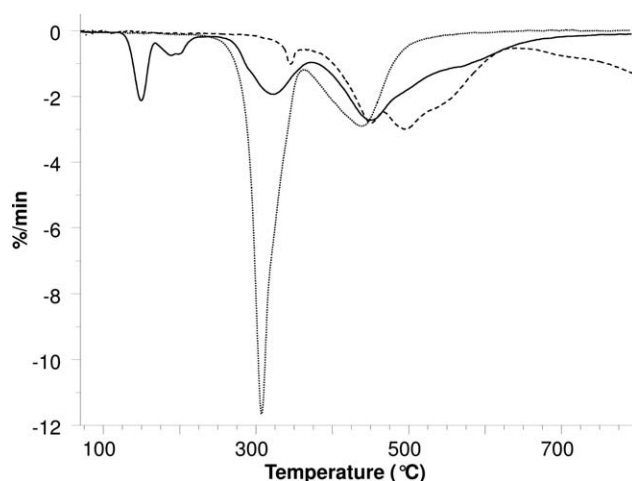


Figure 10. DTG traces of **cBMI** (dashed line), **4F** (dotted line) and **cBMI_n-4F_m** (continuous line).

step with a maximum decomposition rate (PDT) at about 496°C (volatilization rate of −2.9%/min), leaving a stable residue of about 37%. Finally, **cBMI_n-4F_m** (Figures 9 and 10, continuous line) shows a multistep degradation process, starting at about 140°C with two PDT maxima, at about 320 and 450°C, a volatilization rate of −2.0 and −2.8%/min respectively, and the formation of a stable residue at 800°C of about 35.8%.

It is interesting to note a discrepancy between the temperatures of the retro-DA in solution (about 120°C) and in solid state (140°C). The lower temperature recorded in solution respect to solid state is, probably, due the solvent assistance that low the temperature of the retro-DA.

CONCLUSION

In conclusion, we report here the synthesis, assisted by MW irradiation, of a cross-linked polymer whose network structure can be easily degraded by means of a thermal treatment. The process is reversible so that the polymer can be again re-obtained by further MW irradiation. This study is a first step towards the design of new recyclable cross-linked materials, for low-temperature applications, that can be cyclically: formed, degraded, and reused only by thermal treatments.

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