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Some properties of networks produced by the Diels–Alder reaction between poly(styrene-co-furfuryl methacrylate) and bismaleimide

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Abstract

Poly (styrene-co-furfuryl methacrylate) networks were prepared by the Diels–Alder (D–A) reaction in solution at 25 °C between the linear copolymer and bismaleimide (BM). The resultant crosslinked polymers were swollen to equilibrium in toluene at 25 °C and swelling properties were studied by gravimetric and dimensional measurements. The swelling behaviour of these organogels depended on the composition of the copolymer and the concentration of BM used. Shear and Young's moduli and the effective crosslinking densities (ν_e) were determined by compression (stress)–strain measurements. The theoretical crosslinking density was higher than the ν_e for all the crosslinked copolymers. An endothermic peak without T_g was observed on the DSC curve on heating the dry crosslinked polymer. On reheating a T_g at ≈98 °C was found, which is attributed to presence of linear copolymer produced by the retro D–A reaction in the first heating. The thermal stability of a crosslinked copolymer under nitrogen and air showed differences with the stability of the linear copolymer. The increase in viscosity of the solution during the D–A reaction was followed with time, for initial linear copolymers of different molecular weights. It was found that onset of gelation increased to longer reaction times the lower the molecular weight of copolymer.

Keywords: Poly(styrene-co-furfuryl methacrylate); Organogels; Diels–Alder reaction; Swelling; Crosslinking density

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1. Introduction

The Diels–Alder (D–A) reaction has been used extensively in organic synthesis. However, it can also be applied for crosslinking polymers [1–6]. In this reaction a diene reacts with a dienophile to form a cycloadduct [7]. The process can take place at room temperature with no need for a catalyst and on heating it is reversible.

The use of the D–A process to crosslink polystyrene (polyST) has been reported elsewhere [6,8]. Gandini and co-workers [8] prepared a copolymer of ST with a monomer that possesses pendant furan groups. A crosslinked network was formed after addition of a bisdienophile. Canary and Stevens [6], however, synthesised polyST modified with furan and maleimide groups. Admixture of these two polymers also produced a gel.

In our group, copolymers of ST and furfuryl methacrylate (FM) have been prepared [9]. The D–A reaction in solution between this copolymer and 1,1′-(methylenedi-4,1-phenylene) bismaleimide (BM) at room temperature was followed with time by UV [10]. The process was shown to obey second-order kinetics. An increase of the viscosity of the solution was observed during the D–A reaction. However, no experimental analyses were

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then performed to demonstrate this fact [10]. On heating at 77 °C and above, the retro D–A process in the crosslinked poly(ST-co-FM) takes place by a first-order process [11]. The reaction rate at each of the temperatures was obtained and the value of the activation energy was derived [11].

The crosslinked poly (ST-co-FM) is not soluble in those organic solvents that dissolve both copolymer and BM, but it does swell in them. Hence this swollen crosslinked polymer can be termed an organogel. Swelling equilibrium and compression–strain measurements are commonly employed to characterize the behaviour of hydrogels and organogels as described elsewhere [12–16].

As previous studies on this system have focused mainly on kinetic aspects of the D–A and retro D–A processes, it is the main aim of this paper to investigate some properties of crosslinked poly(ST-co-FM) samples, namely, the swelling behaviour, mechanical and thermal properties. In addition, the increase of the viscosity during the D–A reaction will be monitored.

Although there are reports on formation of network polymer systems via the D–A reaction, this paper is, to the best of our knowledge, the first dealing with swelling and elastic properties of polymer networks formed via the D–A process.

2. Experimental

2.1. Materials

ST (Aldrich) was distilled under vacuum and 2,2′-azobis(isobutyronitrile) (AIBN) (Aldrich) was purified by recrystallization from ethanol. Toluene and chloroform rectified (from BDH laboratories) were used without further purification. FM (Aldrich) was purified by high vacuum distillation at 64–66 °C/3 mmHg, cuprous chloride being added to suppress polymerization. BM was obtained from Aldrich.

2.2. Copolymerization

Two linear poly(ST-co-FM) samples were prepared as follows: with toluene as solvent, copolymerization of ST with FM was carried out at 60 °C in sealed tubes under nitrogen, the concentrations of AIBN and of total monomers being 3.5×10^{-3} and 1 mol dm^{-3}, respectively. After a reaction time of 12 h, the tube was cooled and the polymer isolated by precipitation in an excess of petroleum spirit 40–60 °C followed by washing with the precipitant and drying under vacuum at room temperature. Copolymer conversion was ≈10 wt.%.

Four different molecular weight copolymers of the same composition were prepared following the general procedure already explained above. Details of these copolymers are as follows: (a) for three of the samples synthesis was as indicated above, but total monomer concentrations were 4, 6 and 8 mol/dm^3 and the AIBN concentration was 2.5×10^{-3} mol dm^{-3}. The conversions were ≈35–40 wt.%. (b) The last copolymer was prepared in the Dow laboratories, Terneuzen. Copolymerization was carried out up to 85 wt.% of conversion in ethylbenzene (6 wt.%) using 1,1-bis (*tert*-butyl peroxy) cyclohexane (200 ppm) as initiator, *n*-dodecylmercaptan (240 ppm) as the chain transfer and a temperature ramp from 115 to 185 °C.

2.3. Preparation of gels

Admixture of separate solutions in chloroform of copolymer and BM yielded a final concentration of copolymer of 25 wt.%. Five cubic centimetres of the mixed solution was introduced into a test tube at ambient temperature and in contact with air. After most of the solvent had evaporated, a further 5 cm^3 of mixed solution was added. This operation was repeated until a rod of gel of length 25–30 mm was obtained. In between several additions the main mixed solution was kept in the refrigerator to avoid any D–A reaction. The rod of gel produced in the test tube was removed and dried in a vacuum oven at room temperature. Afterwards, the rod was cut into a pellet. The diameter (D_0) and height (L_0) of the pellets were measured using a calliper and a micrometer respectively; and the mass was measured. They were of length 7–10 mm and diameter 8–10 mm. The densities of the dried pellets were obtained from the mass and measured dimensions.

2.4. Swelling measurements

The pellets were swollen to equilibrium in toluene at 25 °C. Toluene was changed regularly to remove any non-reacted material. The swelling equilibrium was attained after approximately four months when eventually constant weight and constant dimensional values were obtained.

The content of copolymer in the organogel can be expressed as a volume fraction, ϕ_2, which is given by the following equation:

$$\phi_2 = \left(\frac{D_0}{D}\right)^3 \tag{1}$$

in which D_0 and D are the diameters of the dry and swollen pellet, respectively. D was measured using a binocular microscope. Graph paper sealed between two thin Perspex discs served as an scale for the measurement of D. This scale was placed at the bottom of a double walled glass container, which was connected to a water bath in order to control temperature. The pellet was immersed in toluene in the container. The microscope was then positioned directly above the pellet to allow direct reading of the diameter to be made.

The volume fraction of toluene in the organogel, ϕ_1, is equal to $(1 - \phi_2)$.

Two of the pellet samples were swollen at four different temperatures. Swelling equilibrium measurements (as described above) were performed within three days after effecting a change to a different temperature.

2.5. Stress (compression)–strain measurements

Elastic moduli of the organogels were determined by stress (compression)–strain measurements in toluene at 25 °C. Descriptions of the compression apparatus and experimental details for its use have been given elsewhere [12].

No barrelling effects were observed during compression.

2.6. Thermogravimetric analyses

Thermogravimetric analyses (TGA) were run with a Mettler TG50 thermobalance analyzer using a heating rate of 10 °C/min. Experiments were performed under atmospheres of air and nitrogen.

2.7. Differential scanning calorimetry (DSC)

Under nitrogen and using a heating rate of 5 °C/min a crosslinked gel sample was treated on a Mettler DSC 30 calorimeter. A first run was performed from 25 to 250 °C. Then, the sample was quenched rapidly to room temperature and a second run was performed up to 250 °C using same heating rate.

2.8. Viscosity change

A U-tube viscometer was used to measure the relative flow time during the D–A reaction at 25 °C using a water bath to maintain constant temperature. Admixture of separate solutions in $CHCl_3$ of a poly(ST-co-FM) sample and BM yielded a 25 wt.% of copolymer in solution and a MI:FM mole ratio equal to 1. Here MI denotes a maleimide group, the molar concentration of which is twice the concentration of BM. Four different M_w copolymers were used. A fixed volume of this solution was then introduced in the viscometer after which the open ends were stoppered. Ten minutes were allowed to attain thermal equilibrium. At different reaction times, the flow time between two fixed marks was read. Relative flow time was taken as the flow time of the solution at a particular reaction time relative to the corresponding quantity at reaction time zero. Except for the period during which flow times were measured, the viscometer was kept stoppered to avoid evaporation of the solvent.

3. Results and discussion

3.1. Linear copolymer

^1H NMR analysis in $CDCl_3$ as described previously [9] gave the mole fraction of FM in each copolymer, F_{FM}, and gel permeation chromatography with universal calibration (courtesy of Dow) was used to measure the molar mass. For two of the copolymers $F_{FM} = 0.0854$ and 0.1354 with M_w equal to 23,000 and 27,000 $g\,mol^{-1}$, respectively. For copolymers all of the same composition ($F_{FM} = 0.0126$) the molar masses were 176,000, 230,000, 365,000 and 540,000 $g\,mol^{-1}$.

3.2. Swelling and mechanical properties

Different organogels were prepared using: (a) the copolymer of $F_{FM} = 0.0126$ (and 540,000 $g\,mol^{-1}$) with five different concentrations of BM, MI:FM mole ratio being 3, 2, 1, 0.5 and 0.25 respectively; (b) the copolymer of $F_{FM} = 0.1354$, MI:FM mole ratio being 1.

All the pellets were found to swell to equilibrium isotropically.

The stress (τ), defined as the applied force per unit area of the undeformed organogel, and the resultant strain $(\lambda - 1)$, where λ is the ratio of deformed to undeformed length of organogel, were obtained from the compression (stress)–strain measurements on the swollen pellets. Values of τ were plotted against the strain. All the plots were linear for low strains, i.e. 0 to ~(0.07–0.08). The value of Young's modulus, E, was obtained from the slope of the linear part.

τ is proportional to $(\lambda - \lambda^{-2})$ as expressed in Eq. (2).

$$\tau = G(\lambda - \lambda^{-2}) \tag{2}$$

where G is the compression shear modulus and is equal to:

$$G = RT\nu_e\phi_2^{1/3}\left[\frac{V_u}{V_f}\right]^{2/3} \tag{3}$$

In Eq. (3) R is the gas constant, T is the absolute temperature, ν_e is the effective crosslinking density and $(V_u/V_f)^{2/3}$ is a correction factor [17] necessary when a solvent is present during the formation of an organogel, as is the case here. V_u and V_f represent the volumes of the dry pellet and of the network at its formation, respectively. V_f is the volume of solution added in the test tube, which is 5 cm^3. V_u can be calculated as the mass (and density) of polymer present in those 5 cm^3 are known.

Plots of τ vs. $(\lambda - \lambda^{-2})$ were linear for low λ values, thus $\lambda < (0.07–0.08)$. The slopes yielded the values of G and using Eq. (3) ν_e was obtained.

ν_e was compared with the theoretical crosslinking density value, ν_t, which is given by the following equation.

$$\nu_t = \left(\frac{N_{\mathrm{FM}}}{V_u}\right)\left(\frac{N_{\mathrm{CFM}} - 1}{N_{\mathrm{CFM}}}\right) \tag{4}$$

In Eq. (4) N_{FM} represents the total number of FM groups in the network and N_{CFM} is the number of FM groups present in each linear polymer chain. V_u has already been defined before. N_{CFM} can be calculated from the copolymer composition and from the number average molar mass value, M_n, as follows:

The calculation of N_{CFM} for the copolymer of $F_{\mathrm{FM}} = 0.0126$ is shown as an example:

The molar mass of the repeat unit in the copolymer chain, M_0, is given as follows, where the molar masses of repeat units of ST and FM are 104 and 166 g mol^{-1} respectively.

$$M_0 = (0.0126 \times 166) + (0.9874 \times 104) = 105\ \mathrm{g\,mol^{-1}}$$

The value of M_n obtained from GPC is 148,000 g mol^{-1}.

The number of repeat units in the copolymer chain is:

$$X_0 = M_n/M_0 = 1409$$

Hence, the number of FM units in the copolymer chain, N_{CFM}, is $1409 \times 0.0126 = 18$.

A value of 22 is obtained for N_{CFM} for the copolymer with $F_{\mathrm{FM}} = 0.1354$. (For this copolymer M_n is 18,000 g mol^{-1}.)

The molar mass per crosslinked unit, M_c, can be calculated via Eq. (5).

$$M_c = \frac{\rho}{\nu_e} \tag{5}$$

The copolymer–toluene interaction parameter χ was calculated from the Eq. (6), which is valid at swelling equilibrium.

$$\ln(1 - \phi_2) + \phi_2 + \chi\phi_2^2 + \nu_e V_1(\phi_2^{1/3} - 2\phi_2 f^{-1}) = 0 \tag{6}$$

in which V_1 is the molar volume of toluene at 25 °C, which has a value of 0.1061 dm^3 mol^{-1} and f is the functionality of BM. f represents the number of elastic chains that emanate from each crosslinked junction. In the present system $f = 4$. BM molecule is small in comparison with the length of the chain between two consecutive reacted FM groups along the copolymer chain (see Fig. 1). This is valid for those copolymers in which the value of F_{FM} is low; otherwise, when the value of F_{FM} is very high, a value of 3 for f would be more correct to consider.

Values of ϕ_2, E, G, ν_e, ν_t, and M_c are listed in Table 1. Some observations can be made:

(i) There is a reasonable anticipated relationship between swellability and ν_e, i.e. those organogels that swell less are those crosslinked copolymers that possess more crosslinking (and hence higher ν_e value) and vice versa.

(ii) In the limit of small deformations, the ratio E/G for an elastic gel should equal 3.0. In extension,

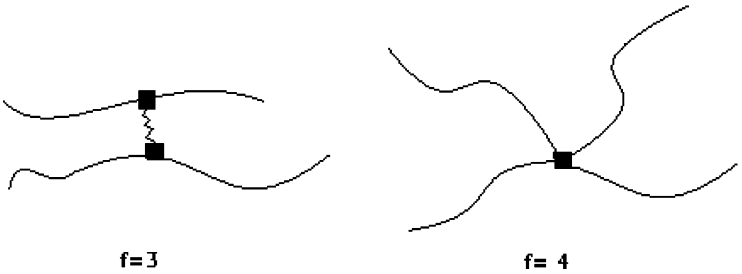

Fig. 1. Schematic representation of the crosslinked junction when f adopts the value of 3 or 4, respectively. (∼) copolymer chain; (〰) BM molecule and (■) crosslinked junction.

Table 1
Values of ϕ_2, E, G, ν_e, ν_t and M_c for crosslinked poly(ST-co-FM) in toluene at 25 °C at swelling equilibrium

F_{FM}	MI:FM	ϕ_2	E (kPa)	G (kPa)	ν_e (mol m^{-3})	ν_t (mol m^{-3})	M_c (10^3 g mol^{-1})
0.0126[a]	3	0.0784	14.6	4.47	20	114	52.3
”	2	0.0843	19.4	5.87	25	114	44.0
”	1	0.1044	43.1	12.9	54	114	20.8
”	0.5	0.0927	25.9	7.93	34	57	32.8
”	0.25	0.0158[b]				28	
0.1354[c]	1	0.3424	581	180	538	1354	2.19

[a] $M_w = 540{,}000$ g mol^{-1}.

[b] Measured using a disc because of fragility of pellet.

[c] $M_w = 27{,}000$ g mol^{-1}.

for small deformations, E/G should be slightly <3.0 and >3.0 for compression [12]. An average value of 3–3.2 has been reported for some hydrogels [12,15,18,19]. In the present work, an average value of 3.3 is obtained.

(iii) The highest modulus is exhibited by the organogel prepared with the copolymer of $F_{\mathrm{FM}} = 0.1354$. The derived value for ν_e for this crosslinked copolymer is the highest. The furan ring within FM is the group that participates in the D–A reaction with the MI unit within BM and consequently the values of ν_e would increase with increasing content of FM in the copolymer.

(iv) The value of ν_e is smaller than that of ν_t for all the crosslinked copolymers; thus not all the furan groups within FM are reacted. This can be explained on the basis of our previous findings [10], in which the reaction between the copolymer and BM was followed and it was shown that: (1) Some BM is not consumed during the formation of the gel. (2) From the BM molecules that have reacted, some molecules have their both MI groups reacted with furan groups yielding crosslinkings and (3) others remain as singly reacted pendant BM molecules (one of the MI groups is reacted and the other group on the same molecule remains free within the network).

In addition, blank experiments were performed in which BM was not added. The formation of a gel was not observed. Therefore, the network formation is due exclusively to the D–A reaction.

Note in Table 1 for those crosslinked copolymers of same composition $\nu_t = 114\ \mathrm{mol\,m^{-3}}$ when a MI:FM mole ratio of 3, 2 and 1 is used. The theoretical number of crosslinkings that might be formed (thus, the number of elastic chains produced) depends on the content of furan groups present in the copolymer as well as on the concentration of BM used to prepare the gels. The composition of the copolymer is fixed. Therefore, the maximum ν_t is achieved when a MI:FM mole ratio = 1 is used. When an excess of BM is used, MI:FM mole ratio > 1, the number of crosslinkings that might be formed will remain the same. However, when FM is in excess, MI:FM mole ratio < 1, the ν_t will differ and its value will depend on the content of BM used.

(v) A linear correlation between concentration of BM used and ν_e is not observed.

The existence of pendant MI groups within the network was found [10] for some crosslinked copolymers ($F_{\mathrm{FM}} = 0.1354$). ^{13}C-NMR analyses yielded the fraction of reacted MI groups within the gels, which was 0.51, 0.66 and 0.78 when a MI:FM mole ratio of 2, 1 and 0.5 was used, respectively. These results showed that the highest crosslinker effectiveness is achieved when a MI:FM mole ratio of 0.5 is used. The same conclusion is reached in the present work despite using a copolymer of different composition ($F_{\mathrm{FM}} = 0.0126$). The ratio ν_t/ν_e equals 5.7, 4.6, 2.1 and 1.6 for the MI:FM ratio of 3, 2, 1 and 0.5, respectively. A low value of this ratio represents a high effectiveness for the crosslinker.

The organogel prepared with a MI:FM mole ratio of 0.25 was extremely soft and difficult to handle; no reliable compression experiments could be performed on this sample. The ν_t value for this organogel is 28 $\mathrm{mol\,m^{-3}}$. Considering the facts described in point (iv), the value of ν_e for this sample must be very low and the corresponding degree of swelling very high (as confirmed by the value of ϕ_2 in Table 1).

(vi) The effect of temperature on the equilibrium swelling was evaluated. Two of the organogels were swollen at four different temperatures. As the temperature increases, the value of ϕ_2 decreases for both samples as shown in Table 2, which shows that the swelling is endothermic over the interval of 15–40 °C. Decreases in ϕ_2 of 43% and 21% are obtained for the samples with $F_{\mathrm{FM}} = 0.0126$ and 0.1354, respectively. This difference could be due to the difference by a factor of ≈10 in the values of effective crosslinking density at 25 °C (see Table 1). A similar situation has been reported [20] for some organogels of crosslinked poly(*N*-vinyl-2-pyrrolidone-co-methyl methacrylate) swollen in dioxan for which the values of ϕ_2 fell on raising temperature from 15 to 61 °C and this decrease was more pronounced for the sample of lowest crosslinking density value.

For the present system it was not possible to study the effect of high temperatures on swelling, as the retro D–A process takes place when the crosslinked copolymer is heated to 77 °C and above [11].

(vii) M_c refers to the molecular mass between two consecutive crosslinking junctions. Theoretically its

Table 2
Volume fraction of copolymer (ϕ_2) in toluene (at swelling equilibrium) at four different temperatures for two organogel samples

Temperature (°C)	ϕ_2	
	$F_{\mathrm{FM}} = 0.0126$[a]	$F_{\mathrm{FM}} = 0.1354$[b]
15	0.118	0.350
25	0.104	0.342
35	0.081	0.336
40	0.067	0.276

[a] $M_w = 540{,}000\ \mathrm{g\,mol^{-1}}$

[b] $M_w = 27{,}000\ \mathrm{g\,mol^{-1}}$

value can be calculated if we assume that: (1) FM units are equidistantly distributed along the polymer chain and (2) all furan groups are reacted. The theoretical value obtained is smaller than the experimental value, for the same reasons already explained in point (iv).

(viii) The value of the polymer–toluene interaction parameter, χ, for the samples with $F_{\mathrm{FM}} = 0.0126$ ranges from 0.326 to 0.397 without any obvious trend with swellability or crosslinking density. However, a comparatively large value of 0.424 is obtained for the sample with $F_{\mathrm{FM}} = 0.1354$. This finding is consistent with the fact that this sample possesses the highest crosslinking density and the lowest affinity for solvent as indicated by the value of ϕ_1.

(ix) The values shown in Tables 1 and 2 cannot be compared with literature values as such studies on thermally reversible polymers via the D–A reaction have not been reported. There is one report [2], in which hydrogels were prepared by the D–A reaction between furan and MI modified polyoxazolines. Swelling degree was defined as the mass of water in the swollen hydrogel divided by the mass of dried hydrogel. The values are in the range of 1 to 14. The swelling degree depended on the content of furan and MI groups that were present in the starting polymers. The lowest content of both groups was 4 mol% and the highest was 21 mol%. The authors observed a decrease in swelling degree when the content of reactive groups in polymers increased. In the present work, the range of values for the swelling degree as defined by Chujo et al. [2] is 0.96–9.5.

3.3. Thermal properties

The thermal stability of a crosslinked poly(ST-co-FM) sample (with $F_{\mathrm{FM}} = 0.0856$, $M_{\mathrm{w}} = 23{,}000\ \mathrm{g\,mol^{-1}}$ and a MI:FM mole ratio equal to 1) was studied and compared with that of the original linear copolymer as shown in Fig. 2. The main features are: (i) there is a first step, from 130 to 350 °C, in which the linear copolymer shows better stability than the crosslinked sample in both, air and nitrogen, atmospheres. The copolymer itself, due to the presence of FM moieties, presents poorer thermal stability than poly-ST as described in a previous paper [9]. In addition, BM was heated under nitrogen up to 600 °C. From 25 to 300 °C a loss of ≈4 wt.% was observed; (ii) in the final stage of the degradation, the crosslinked sample displays a more stable behaviour. In air a 100 wt.% loss occurs eventually, whereas in nitrogen 7 wt.% of the original crosslinked gel sample remains undegraded even at 600 °C, which could be due to the BM moiety. This molecule itself suffers only around 45% of weight loss at such high temperature.

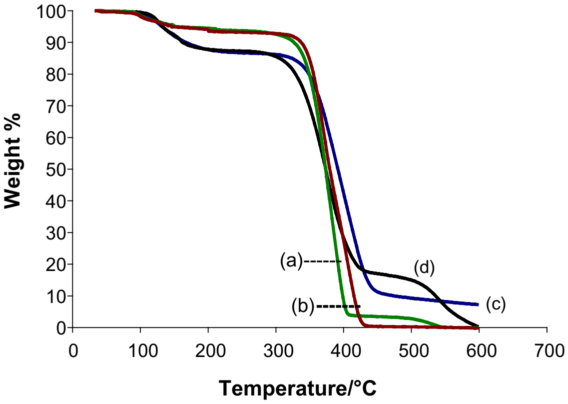

Fig. 2. TGA curves for the linear copolymer of $F_{\mathrm{FM}} = 0.0856$ (with $M_{\mathrm{w}} = 23{,}000\ \mathrm{g\,mol^{-1}}$): (a) in air, (b) in nitrogen and for the crosslinked copolymer, (c) in nitrogen and (d) in air.

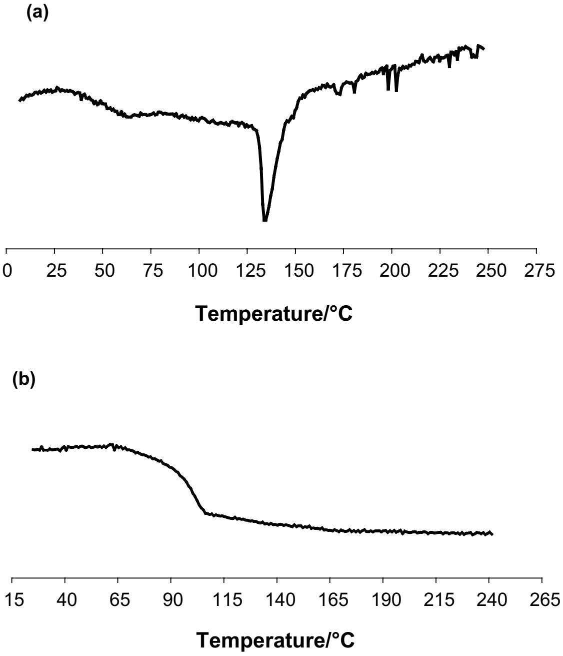

Fig. 3. DSC curves for a crosslinked poly(ST-co-FM) sample (with $F_{\mathrm{FM}} = 0.0126$, $M_{\mathrm{w}} = 540{,}000\ \mathrm{g\,mol^{-1}}$ and a MI:FM mole ratio of 1): (a) First run and (b) a consecutive second run.

A crosslinked poly (ST-co-FM) sample (with $F_{\mathrm{FM}} = 0.0126$, $M_{\mathrm{w}} = 540{,}000\ \mathrm{g\,mol^{-1}}$ and with a MI:FM mole ratio of 1) was run on DSC. Fig. 3a shows the DSC curve for the first run. There is no evidence for a glass transition temperature, but an endothermic peak is observed at 135 °C. Fig. 3b corresponds to the second run, in which a transition is observed around 98 °C. The D–A reaction is reversible on heating. This reverse reaction produces the reactants, in the present work, the linear copolymer and BM [11]. Therefore, the transition at 98 °C is very likely to correspond to the T_g of the reformed linear copolymer, which accords with the values of T_g found for linear poly (ST-co-FM) samples [9].

Chen et al. [21,22] prepared highly crosslinked networks by D–A reaction between a monomer that possesses four furan moieties and: (i) monomer with three MI groups [21] and (ii) monomers with two MI end groups [22]. They performed also some DSC experiments on their crosslinked samples and found endothermic transitions starting at 120 °C.

3.4. Viscosity change

During the D–A reaction between poly (ST-co-FM) and BM the viscosity of the solution medium increases with reaction time.

The change of the viscosity was followed by measurements of the relative flow times. Four different molecular weight copolymers were used (of same composition $F_{FM} = 0.0126$ and with a MI:FM mole ratio of 1). Fig. 4 illustrates the relative flow times (defined in Section 2.8) vs. the reaction time for each of the samples. Quantitative analysis would be extremely complex in view of the changing nature, composition and linearity of the system. However, it may be observed that all the curves display a common feature: the relative flow time increases smoothly in the beginning. Afterwards it increases more rapidly, reaching eventually a time at which experimentally is was not possible to make more measurements. At this stage, the solution was very viscous. The differences found are that the lower the M_w of the copolymer used, the longer the reaction time to reach that stage at which the solution becomes extremely viscous. This sequence seems reasonable, since a small proportion of crosslinking for the start of gelation is necessary for high molecular weight polymers [23]. In addition, the N_{CFM} value is higher for the copolymer of high M_w and therefore, for this copolymer the condition for branching and later crosslinking is better achieved [24]. The gel point for the copolymer of $M_w = 540,000$ g mol^{-1} is 100 h [11], which is the time at which experimentally no more measurements could be performed (see Fig. 4a). Therefore, it seems correct to affirm that the gel point will be achieved at longer times the lower the molecular weight of the copolymer used.

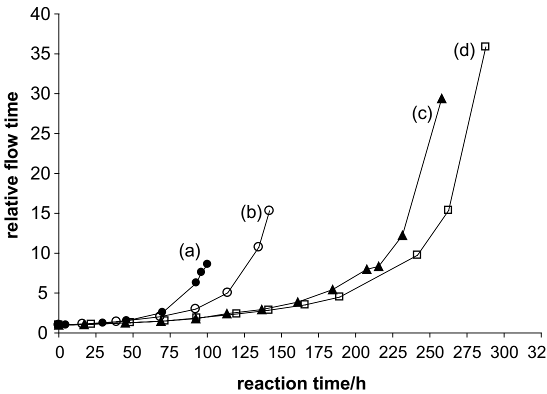

Fig. 4. Relative flow times vs. reaction time during the D–A reaction between poly(ST-co-FM) and BM with a MI:FM mole ratio of 1, at 25 °C in $CHCl_3$ for four different molecular weight copolymers (with F_{FM}=0.0126). (●) 540,000 g mol^{-1}, (○) 365,000 g mol^{-1}, (▲) 230,000 g mol^{-1} and (□) 176,000 g mol^{-1}.

4. Conclusions

1. The highest Young's modulus is exhibited by the organogel prepared with the copolymer of $F_{FM} = 0.1354$ and this crosslinked copolymer possesses the highest effective crosslinking density.
2. The effective crosslinking density is lower than the theoretical value for all the crosslinked copolymers.
3. Among the crosslinked copolymers prepared in the presence of different BM concentration, the highest crosslinker effectiveness is achieved when a MI:FM mole ratio of 0.5 is used.
4. A temperature increase produces an increase in the content of toluene in the swollen organogel, i.e. swelling is endothermic.
5. An endothermic peak without T_g was observed on the DSC curve on heating the crosslinked polymer. On reheating a T_g at ≈98 °C was found. This is attributed to regeneration of the linear copolymer via the retro D–A process in the first heating.
6. The present organogels could be used at room temperature. However their application at high temperatures is restricted, as the retro D–A reaction transforms the crosslinked copolymer into linear copolymer.

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