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Some observations on the copolymerization of styrene with furfuryl methacrylate

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Abstract

The tendency for crosslinking to occur either during free radical polymerization in solution or to develop subsequently in air after precipitation of linear polymer has been observed for both polymerization of furfuryl methacrylate (FM) and copolymerization of FM with styrene (ST). Reactivity ratios $r_{FM} = 0.33 \pm 0.08$ and $r_{ST} = 0.44 \pm 0.02$ have been determined. Thermo-oxidative stability is lowered by incorporation of FM moieties into poly-ST. Glass transition temperatures (T_g) of copolymers accord with the Fox equation and extrapolation affords a value of 64°C for the T_g of linear poly-FM. After admixture of solutions of poly(FM-co-ST) and bismaleimide (BM) at ambient temperature crosslinked gel is produced slowly by intermolecular Diels–Alder reaction between diene units (FM) and the dienophile (BM). The retro Diels–Alder reaction occurs rapidly on heating, regenerating linear copolymer and BM. The crosslinked gels exhibit considerable swelling in chloroform and toluene. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Poly(furfuryl methacrylate-co-styrene); Reactivity ratios; Thermoreversible crosslinking

1. Introduction

Early studies [1] indicated that free radical initiated polymerization of furfuryl esters of acrylic and methacrylic acid yields insoluble, crosslinked products. Subsequently, this observation was confirmed [2,3] for the polymerization in bulk of furfuryl methacrylate (FM). In solution, polymerization of FM is reported in a few studies [4,5] to yield linear polymer. Both in bulk [6,7] and in solution [5,7,8], copolymerizations involving FM appear to afford only linear products and, in one instance [7], this occurred at low as well as high conversion. Several asserted possible applications of poly-FM and copolymers containing FM have been proposed [3]. None of these coincides with the ultimate aim of the present research, which is to introduce FM moieties into a polymer and exploit the diene character by subsequent post-polymerization, Diels–Alder reaction with a dienophile to produce crosslinking that is thermally reversible.

Some preliminary attempts here to produce poly(FM-co-ST) in solution led to crosslinking at medium–high content of FM in the feed. In contrast, Goh et al. [8] were able to derive reactivity ratios in copolymerization systems of FM with ST, *p*-methyl-ST and acrylonitrile in which the highest mole fraction of FM in the feed was 0.87, 0.78 and 0.93, respectively. In the present communication the FM/ST system is re-examined from the standpoint of synthesis and stability of copolymers and the feasibility of participation of the copolymers in a gel-forming process is also examined.

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 rectified (from BDH laboratories) was 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. 1,1′-(methylenedi-4,1-phenylene) bismaleimide (BM) (95%) was obtained from Aldrich.

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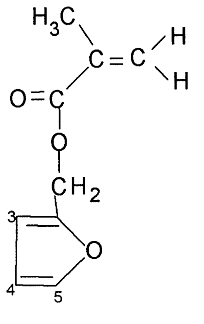
The formula of FM is as follows and that of BM appears later:



FM

2.2. Physicochemical measurements

The refractive index of FM at a wavelength 589 nm was measured using an Abbé refractometer thermostated at several temperatures via an external water bath and a DMA 55 digital density meter calibrated with air and water was used for density measurements over a range of temperatures. Infrared spectra were measured using a Perkin Elmer 1710 infrared Fourier transform spectrometer. Composition of the copolymers was determined by H-NMR using solutions in $CDCl_3$ with a Bruker 300 MHz instrument.

Glass transition temperatures (T_g) of copolymers were measured under nitrogen with a Mettler DSC 30 calorimeter, using a heating rate of 5°C/min. T_g was taken as the midpoint value of the transition curve. Thermogravimetric analyses (TGA) of samples were made with a Mettler TG50 thermobalance analyser using a heating rate of 10°C/min. Experiments were run in air.

2.3. Polymerization of FM

With toluene as solvent, polymerization of FM was carried out at 50°C in sealed tubes under nitrogen. Initially, different monomer concentrations and an AIBN concentration of 1.5×10^{-2} mol/dm^3 were used, but in all experiments a gel was observed in the tube during polymerization. Later, gel formation was prevented by reducing the monomer concentration to 1 mol/dm^3. After selected reaction times, 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.

2.4. Copolymerization

Procedures and conditions were similar to those adopted for polymerization except for the use of 60°C, concentration of AIBN 3.5×10^{-3} mol/dm^3 and concentration of total monomers being 1 mol/dm^3 for all feed compositions. Copolymer conversions were ca. 10% and, in general, the time to attain such conversions increased with increasing content of FM in the feed.

2.5. Copolymers

To assess stability after formation, a precipitated washed copolymer sample was partially dried for a few hours at room temperature. Then at various times a tared portion was subjected to Soxhlet extraction with chloroform for 16 h (previously verified to be adequate) after which the thimbles were dried to constant weight, thereby yielding the mass (if any) of crosslinked material produced in a post-polymerization period at room temperature.

To assess thermal stability in air, a weighed sample of copolymer was placed in an oven at 240°C in an air atmosphere for 1 h, after which the sample was weighed and examined by IR.

3. Results and discussion

3.1. FM

The linear dependences of density ρ (g/cm^3) and refractive index (n) on temperature, T (°C), were, respectively:

$$\rho = 1.0817 - 0.001(T - 25), \qquad R^2 = 0.999$$

$$n = 1.4779 - 0.0005(T - 25), \qquad R^2 = 1$$

It was noted that, at any temperature, the values of ρ and n were smaller by ca. 0.016 g/cm^3 and 0.004, respectively, than the corresponding values for unpurified FM.

FM is not a frequently used monomer and it was considered useful to measure these physical properties, which do not appear to have been reported before. Moreover, they were used here as a check of purity following vacuum distillation of each batch of FM.

3.2. Polymerization of FM

After reducing finally the monomer concentration to 1 mol/dm^3 the initial precipitated polymer at various times was found to be soluble in chloroform. Following an induction period of 14 h the percentage of conversion increased rapidly to a value of 94% at 23 h, the plot being suggestive of autoacceleration. It was not possible to make a comparison of approximate rates with literature values. In the only related study [2], a different technique for following the reaction was used, polymerization was in bulk rather than in solution. The concentration of initiator and temperature also differed from those used here and, although plots were reproduced, the values of the rates (% conversion/time) were not quoted.

Linear polymer was found to develop crosslinking on standing in air after isolation by precipitation, as evidenced by the results of Soxhlet extraction for a linear poly-FM sample produced at 50% conversion. Fig. 1, in which

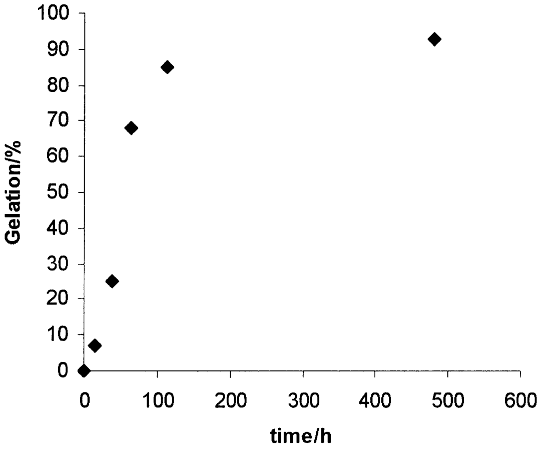


Fig. 1. Variation of percentage of post-polymerization gelation with time for poly-FM.

'time' means the period of standing at room temperature prior to Soxhlet extraction, shows a strong increase of gelation with time. After 500 h, ca. 90 wt % of initially linear polymer is in an insoluble crosslinked form.

3.3. FM-ST copolymers

Attempts to prepare and analyse copolymers covering the whole span of feed composition were vitiated by the same type of post-polymerization crosslinking that was found in homopolymerization, i.e. development of gelation with time after isolation of linear polymer. This effect was more pronounced the higher the mole fraction of FM in the feed, f_{FM}. Thus with $f_{FM} = 0.652$ the precipitated copolymer was soluble in chloroform, but its insolubility due to gelation developed with time thereafter. Samples that remained free from crosslinking and hence suitable for NMR analysis were provided at low–medium values of f_{FM}.

NMR analysis yielded the instantaneous mole fractions of FM and ST (F_{FM} and F_{ST}, respectively) in the copolymer. The calculation of composition was based on the ratio of the intensity of resonance from the phenyl protons, I_{ST} ($\delta = 6.5$–7.2 ppm) to the intensity due to the two furfuryl protons 3 and 4 (of the furan ring), I_{FM} ($\delta = 6.0$–6.4 ppm).

$$\frac{I_S}{I_{FM}} = \frac{5F_{FM}}{2F_{ST}} \qquad (1)$$

Also, it holds that: $F_{FM} + F_{ST} = 1$. For those copolymers prepared with a very low content of FM ($f_{FM} < 0.038$) in the feed NMR was not sufficiently sensitive and for these cases, elemental analysis (percentage of C, H and thereby percentage of O) was used instead. Table 1 lists the values of f_{FM} and F_{FM}.

Table 1
Values of F_{FM} and f_{FM} for S–FM copolymers

f_{FM}	F_{FM}
0.026	0.055[a]
0.038	0.072[a]
0.05	0.093
0.074	0.114
0.114	0.175
0.136	0.224
0.155	0.239
0.187	0.280
0.214	0.304
0.258	0.330
0.273	0.344
0.298	0.370
0.298	0.356[a]
0.371	0.388
0.384	0.398
0.426	0.470
0.489	0.458
0.492	0.461
0.536	0.496
0.605	0.544

[a] Measured by elemental analysis.

The Extended Kelen–Tüdős [9] and Mao–Huglin [10] methods were used to evaluate the reactivity ratios. Both involve not only copolymer compositions but also the values of the fractional conversion. The M–H method is an iterative method, the component steps of which involve the K–T procedure. The 95% confidence limits of the values of the reactivity ratios r_{FM} and r_{ST} give an idea of the experimental error and they may be calculated by the confidence interval estimation technique of the linear least-squares method. Full details of the procedures involved in evaluating the reactivity ratios and uncertainty limits with relevant ellipses have been published previously [11]. For both K–T and M–H procedures the results are: $r_{FM} = 0.33 \pm 0.08$ and $r_{ST} = 0.44 \pm 0.02$. These are not dramatically different from the values of $r_{FM} = 0.42 \pm 0.01$ and $r_{ST} = 0.34 \pm 0.03$ obtained by Goh et al. [8], whose feed compositions extended to higher values of f_{FM} than was possible here. These authors made no mention of crosslinking or post-polymerization gelling.

The values of the reactivity ratios yield $0 < r_{ST} \cdot r_{FM} < 1$, which means that the comonomer units are distributed randomly in the copolymer. As both values are less than unity, the ST–FM system has an azeotropic feed composition, $(f_{FM})_c$ that is given by Eq. (2):

$$(f_{FM})_c = (1 - r_{ST})/(2 - r_{FM} - r_{ST}) \qquad (2)$$

Hence the value of $(f_{FM})_c$ is 0.455.

The compositional drift of copolymer with fractional conversion θ was examined by means of the Meyer–Lowry procedure [12]. Full details and relevant equations have been published by us previously [13,14]. Calculated curves for various initial feed compositions are shown in Fig. 2, where curve 4 (azeotropic composition) represents, of course, no change in instantaneous copolymer composition F_{FM} and no change in F_{FM} with θ. The compositional drift is quite small in the vicinity of the azeotrope, i.e. $f_{FM} = 0.4 - 0.6$. At high contents of FM in the feed (e.g.

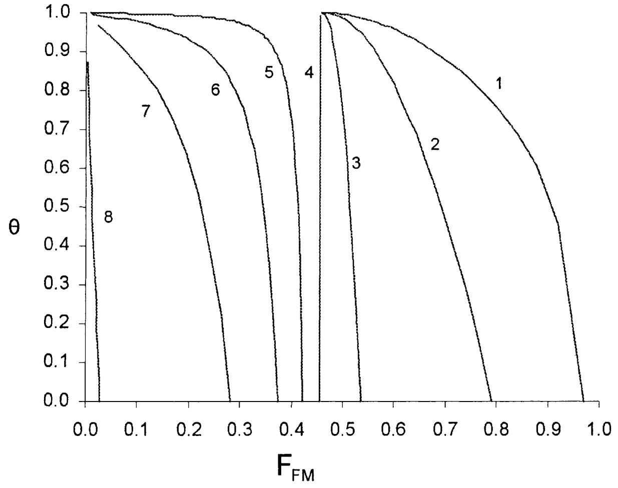


Fig. 2. Calculated curves of fractional conversion vs. instantaneous mole fraction of FM in the copolymer for the FM-ST copolymerization. Curves 1–8 relate to initial feed compositions f_{FM} of 0.99, 0.9, 0.6, 0.455, 0.4, 0.32, 0.2 and 0.013, respectively. Curve 4 is the case $f_{FM} = (f_{FM})_c$.

curve 1) $F_{FM} < f_{FM}$ and the drift in copolymer composition with θ is considerable. For end-use it is important that the fundamental properties of PS be essentially unchanged and hence copolymers of low content of FM are preferred. It is seen (e.g. curve 8) that in this case $F_{FM} > f_{FM}$ and in absolute terms the compositional drift with conversion is smaller than exists at high contents of FM in the feed.

3.3.1. Thermal analysis

Table 2 lists the measured values of T_g for polystyrene and eight copolymers of different composition. In the Fox expression (Eq. (3)) W denotes weight fraction.

$$\frac{1}{T_g} = W_{ST}\left(\frac{1}{T_{gST}} - \frac{1}{T_{gFM}}\right) + \frac{1}{T_{gFM}} \tag{3}$$

The plot of $1/T_g$ vs. W_{ST} (not illustrated) is accurately linear and extrapolation to $W_{ST} = 0$ yields 64°C as the T_g of poly-FM. The copolymers used extended to a maximum content of FM of $W_{FM} = 0.556$, i.e. those which did not crosslink during their synthesis. The data of Goh et al. [8] extended to higher contents of FM, i.e. up to $W_{FM} = 0.91$ ($T_g = 64$°C) and extrapolation to $W_{ST} = 0$ yields 66°C as the T_g of poly-FM. It is not evident and is contrary to our experimental observations how Goh et al. were able to obtain non-crosslinked samples of poly(FM-co-ST) at high contents of FM. Nonetheless, it remains significant that their data and the present ones afford rather similar extrapolated values for the T_g of poly-FM.

TGA analyses run under an atmosphere of air for polystyrene and three copolymers have the following features: (i) thermo-oxidative stability of polystyrene is decreased when FM moieties are introduced, (ii) the degradation of polystyrene follows a one-step process, whereas more than one stage occurs for the copolymers; this is particularly evident for the sample of highest content of FM, (iii) 100% weight loss, i.e. total degradation, occurs eventually for all the samples, which differs from the situation prevailing in an atmosphere of nitrogen, when weight loss does not exceed ca. 90% even at 500°C [8].

Table 2
Values of T_g for some S–FM copolymers. W_{FM} represents the weight fraction of FM in copolymer

W_{FM}	T_g (°C)
0	99
0.032	94
0.100	93
0.113	90
0.201	89
0.315	88
0.466	80
0.499	79
0.556	78

Because processing of unmodified poly-ST is normally conducted in air at ca. 240°C, possible changes in poly(ST-co-FM) were investigated in air at this temperature and also, for comparison, in air without heating. The samples having $F_{FM} = 0.49$ were placed in air oven and examined by IR as a mull in Nujol. The spectra for the two cases were similar except for the appearance of peaks at 1690, 1740 and 1798 cm^{-1} in the sample that has been heated. As suggested elsewhere [4], these are likely to be due to the formation in the FM units of 2,4-dimethyl glutaric anhydride structure.

3.4. Gelation

The gelation noted during the polymerization of FM in solution could be suppressed by reducing the initial concentration of monomer. Similarly, by reducing the initial concentration of total monomers (irrespective of feed composition) gelation could be suppressed during copolymerization. Crosslinking during synthesis has been noted by other workers [15,16] who attributed its occurrence to lability of the carbon-5 of the furan ring, facilitating attack by radicals and eventual formation of a crosslinked network structure. However, crosslinking after synthesis has also been observed in poly-FM and poly(FM-co-ST) having high contents of FM. Such samples develop a yellow–brown coloration and insolubility, which increase with time. Canary and Stevens [15] modified poly(ST-co-maleic anhydride) by attaching pendant furfuryl groups. These polymers in solution became dark and eventually gelled with time. Similar types of finding were reported by Goussé et al. [16], who prepared copolymers of ST with a novel comonomer possessing a furfuryl group. The effects were more marked the higher the content of the comonomer. This behaviour was attributed to the lability of a hydrogen atom of the methylene group attached to the furan ring. It was proposed that removal of this atom can lead to intermediates (two ionic and one free radical), which are stabilized by the dienic

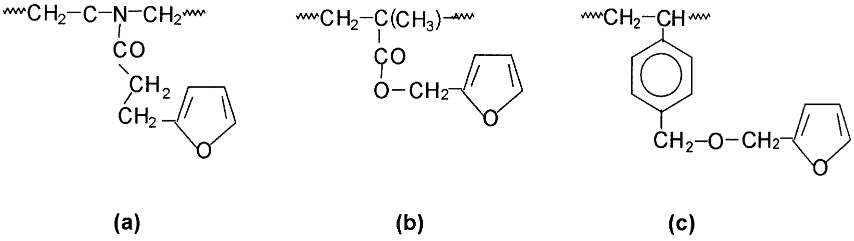


Fig. 3. Dienic monomer units in the copolymers (a) Chujo et al. [17], (b) present work, (c) Goussé et al. [16]. For discussion see text.

character of the furan ring. Coloration and gelation in air were overcome when the polymers were stored under nitrogen.

To investigate the existence and/or role of a stable free radical some of our poly(ST-co-FM) samples of various contents of FM were examined by electron spin resonance (courtesy Dr J.P. Zhao, University of Manchester). However, no spectra characteristic of radical species could be found.

The observation above on the labile hydrogen atom of the methylene group appears to be supported by the findings of Chujo et al. [17], who prepared, as possible precursors to a D–A reaction, two separate polymers based on poly(*N*-acetylethylenimine) (PAEI). One of these was PAEI modified with furan. When stored as solutions in the dark no stability problems ensued. Denoting the systems of Chujo et al., the present work and Goussé et al. by (a), (b) and (c) respectively, the sequence of stability is observed experimentally to be (a) > (b) > (c). The relevant formulae in the three cases, which are shown in Fig. 3, are useful in correlating stability with structure as discussed below:

(i) all three monomer units contain a furfuryl group.
(ii) the lability of the $-CH_2$ of the furfuryl group is high in (b) and (c) because of both the acyl oxygen and furan group attached to it in (b) and the ether oxygen and furan group in (c).
(iii) in (a) the ether oxygen is absent; hence lability is lowered and overall stability of polymer increases.
(iv) lability is lowered somewhat also by the carbonyl group present in (a) and (b), but not in (c).

We have observed that these copolymers (mostly those with high amount of FM) develop a yellow colour when standing for a long time (several weeks) in contact with air. When discussing furfural, Zeitsch [18] explains that oxygen abstracts the hydrogen atom at the 5-position of the furan ring, thus producing a radical on it which may continue attacking other double bonds, leading after reformation to a number of double bonds. These bonds are responsible for the colour build up by an increase in the wavelength of the light absorbed. This might explain the colour observed in our copolymers.

3.5. Diels–Alder (D–A) crosslinking

We report finally a preliminary experiment designed to introduce crosslinking deliberately. A solution in toluene of poly(FM-co-ST) having $F_{FM} = 0.05$ was added to a solution in toluene of BM having a stoichiometric content of BM with respect to the FM in the copolymer. In this mixture the concentration of copolymer was 12 wt%. After admixture of the two solutions and stirring, the resultant homogeneous solution was left in contact with air at 25°C. An increase in viscosity was observed and after 12 days the material was so viscous that it remained immobile on inverting the sealed test tube. The material was removed and more toluene added to yield a swollen gel. On heating under reflux to 110°C the swollen crosslinked polymer had reverted to a solution after 1 h. The solution was concentrated by evaporation of some of the toluene and then left at room temperature. Crosslinked gel developed after several days. Under the conditions adopted, the uncatalysed D–A reaction at ambient temperature is slow, whereas the retro D–A reaction is rapid (see Fig. 4).

To determine the degree of swelling in the crosslinked gel an experiment similar to that indicated above was conducted but with the use of chloroform (instead of toluene) as solvent because of its greater volatility. A portion of the mixed solution was introduced into a plastic cap at ambient temperature and in contact with air. After most (but not all) of the solvent had evaporated, a further portion of mixed solution was added. In between several additions the main mixed solution was kept in the refrigerator to avoid any D–A reaction. This disc of gel produced in the plastic cap was removed and dried in a vacuum oven at room temperature. The diameter and mass of the disc were measured in the dry state and also after equilibrium swelling in chloroform had been attained in 5 days. The resultant equilibrium solvent contents of organogel were 88 vol% and 90 wt%.

It was confirmed in a blank experiment, in which a solution of copolymer alone (i.e. in absence of BM) was left in air, that crosslinking did not occur. Hence it can be inferred with confidence that with BM the crosslinking was due to a D–A reaction. Of course the deliberately induced crosslinking reaction involved the use of a copolymer having a low content of FM. As noted previously, solid samples of high content of FM develop crosslinking with time in air. It remains to be investigated whether the D–A induced crosslinking occurs in air between such copolymers and BM and it is also proposed to study the kinetics of the D–A process.

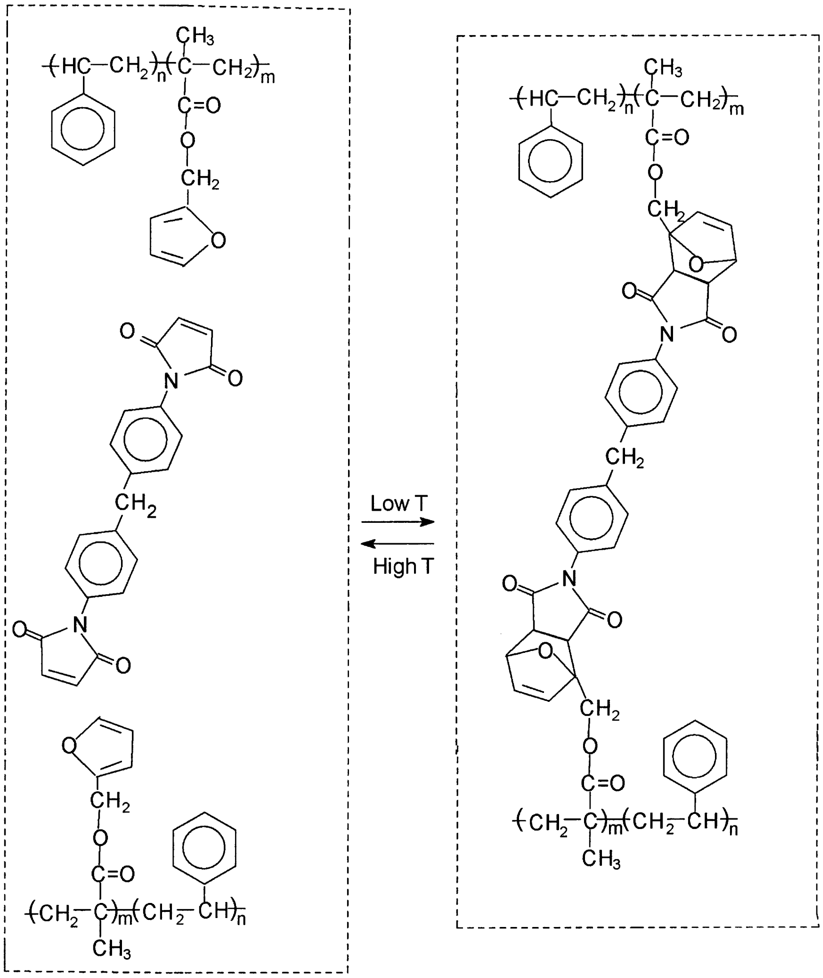


Fig. 4. Representation of the crosslinking of S-FM copolymer with BM.

4. Conclusions

1. Linear poly-FM can be produced by polymerization in dilute solution, but crosslinking of the solid samples develops subsequently on storage in air. The interpolated T_g of the polymer is 64°C.
2. Similar considerations apply to synthesis and stability of poly(ST-co-FM) especially at high contents of FM. For this copolymerization the reactivity ratios are: $r_{FM} = 0.33 \pm 0.08$ and $r_{ST} = 0.44 \pm 0.02$.
3. Thermo-oxidative stability of poly(ST-co-FM) is lower than that of poly-ST and eventual weight loss in the copolymer is greater than that which occurs for degradation in nitrogen.
4. The feasibility of inducing crosslinking on air at ambient temperature has been demonstrated by the D–A reaction in solution between poly(ST-co-FM) and BM. The network is broken down by the retro D–A reaction at 110°C. The dry crosslinked gels swell to yield organogels of approximately 90% equilibrium solvent content.
5. Several of the present findings suggest that it is advisable to approach with caution certain possible applications (e.g. biomaterials) proposed [3] for poly-FM and FM-containing copolymers.

Acknowledgements

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