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The Thermal Stability of Cross-Linked Polymers: Methyl Methacrylate with Divinylbenzene and Styrene with Dimethacrylates

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Abstract

Cross-linking of polymers is frequently presumed to enhance the thermal stability of polymer systems. Methyl methacrylate has been reacted with divinylbenzene and styrene with various dimethacrylates. These systems have been characterized by gel content, swelling ratio, infrared spectroscopy, thermal analysis, TGA/FT-IR, and solid state NMR. Both systems show enhanced thermal stability and char formation. This is most pronounced in the cases of methyl methacrylate with divinylbenzene and styrene with bisphenol A dimethacrylate.

Keywords

Thermal stability, Cross-linking, Methyl methacrylate, Styrene, Divinylbenzene, Dimethacrylates

1. Introduction

Research on the correlation between cross-linking and the thermal stability of polymers, using various cross-linking procedures, has been a focus for this group for a number of years. Epoxy resins have been shown to have a thermal stability that is independent of cure conditions and therefore on cross-link density [1]. Other resins have been shown to have an increase in char formation and decrease in flammability (increase in thermal stability) as the amount of cross-linking is increased [2]. It has been shown that polyamide-6 irradiated with ^{60}Co - γ -rays can form intermolecular cross-links [3]. However this does not lead to enhanced thermal stability, a decrease in the onset temperature of degradation is observed for polymers cross-linked by irradiation versus the unirradiated polyamide-6 [3]. Polybutadiene has been shown to undergo cross-linking under an inert atmosphere in a thermogravimetric analyzer where the cross-link density is dependent upon the temperature and time [4]. Polybutadiene (PBD), polystyrene, K-resin, and SBS undergo cross-linking upon irradiation with ^{60}Co - γ -rays [5]. Polybutadiene shows a decrease in thermal stability upon irradiation while polystyrene shows an increase in thermal stability and the copolymers (K-resin and SBS) have a thermal stability that is related to the amount of PBD present. This decrease in thermal stability for polybutadiene cross-linked by irradiation compared to thermally cross-linked polybutadiene is thought to be due to irradiation induced fragments that can be easily evolved upon thermal degradation [5].

As can be seen from the above work, no direct correlation between cross-linking and thermal stability has been clearly established. We have previously reported the relationship of cross-link density and thermal stability for methyl methacrylate cross-linked with various dimethacrylates and styrene cross-linked with divinylbenzene [6]. Cross-linked styrene–divinylbenzene polymers have a significant cross-link density and show a pronounced enhancement in thermal stability and an increase in char formation. On the other hand, methyl methacrylate–dimethacrylate cross-linked polymers did not show an increase in thermal stability even though they have a high cross-link density. It is thought that the aromatic character of the styrene–divinylbenzene cross-linked polymers was responsible for the enhanced thermal stability.

The focus of this paper is the copolymerization of methyl methacrylate with divinylbenzene and styrene with various dimethacrylates by a chemical means. The relationship between this work and previous work involving methyl methacrylate and styrene will provide us with more insight to the factors responsible for thermal stability.

2. Experimental

2.1. Materials

All reagents including anhydrous chloroform and anhydrous tetrahydrofuran (THF) were obtained from Aldrich Chemical Company. The monomers were purified by passing the monomer through a column packed with an inhibitor remover (supplied by Aldrich Chemical Company). Azobisisobutyronitrile, AIBN, was recrystallized from methanol.

2.2. Analysis

Thermogravimetric analysis was done on a Mettler 3000 thermoanalyzer at a scan rate of 10°C per min, in both argon and air atmospheres. Infrared spectra were obtained using a Nicolet Magna infrared 560 spectrometer E.S.P. TGA/FT-IR were performed on a Cahn TG-131 balance interfaced to a Mattson Galaxy Fourier transform infrared spectrometer under inert atmosphere at a scan rate of 20°C per min. Solid state NMR spectroscopy was carried out using a Bruker MSL spectrometer operating at a frequency of 25 MHz for carbon. All experiments were carried out using cross polarization (CP) and magic angle spinning (MAS) at a frequency of 5 kHz. Spinning sidebands accounted for 6% of the total aromatic carbon. A recycle delay of 2 s was used for experiments. The CP-MAS contact time was varied in order to determine the optimal contact time; this was found to be 1 ms and this was used for all experiments.

2.3. Polystyrene

Into a 100-ml round-bottomed flask was placed 10.00 g of styrene, 0.18 g of AIBN, and 40 ml of chloroform and this was heated to reflux with stirring for 24 h. The polymer was precipitated with methanol and then dried in a vacuum oven overnight.

2.4. Styrene/dimethacrylate copolymers

Into a 100 ml round-bottomed flask was placed 6.02 g of styrene, 4.03 g of ethylene glycol dimethacrylate, 0.170 g of AIBN, and 40 ml of chloroform and this was heated to reflux with stirring until a gel formed and the stir bar could no longer move. The gel was collected by vacuum filtration and rinsed with chloroform and then dried in a vacuum oven overnight. Then the solid was extracted with tetrahydrofuran and the gel content and swelling ratios were determined.

The above procedure was followed for all of the following dimethacrylates: ethylene glycol dimethacrylate (EGDMA); bisphenol A dimethacrylate (BADMA); hexamethylene glycol dimethacrylate (HMGDMA); neopentyl glycol dimethacrylate (NGDMA). The amount of dimethacrylate was varied from 10 to 40 wt.% in 10% increments.

2.5. Poly(methyl methacrylate)

Into a 100 ml round-bottomed flask was placed 10.00 g of methyl methacrylate, 0.18 g of BPO, and 40 ml of toluene and this was heated to reflux with stirring for 24 h. The polymer was precipitated with methanol and then dried in a vacuum oven overnight.

2.6. Methyl methacrylate/divinylbenzene copolymers

In a typical experiment, into a 100 ml round-bottomed flask was placed 4.05 g of divinylbenzene, 6.02 g of methyl methacrylate, 0.110 g of BPO, and 40 ml of toluene and this was heated to reflux until gel formed and stir bar could no longer move. The gel was collected by vacuum filtration and rinsed with toluene and then dried in a vacuum oven overnight. Then the solid was extracted with tetrahydrofuran and the gel content and swelling ratios were determined. The percentage of divinylbenzene was varied from 10 to 40 wt.% in 10% increments.

2.7. Determination of gel content and swelling ratio

Gel content and swelling ratios were determined by extracting the dried cross-linked polymers in tetrahydrofuran using a Soxhlet extraction apparatus. Polymers were extracted for 12-h periods. After removal from the Soxhlet apparatus, the sample was patted dry and mass determined. The cross-link density of the samples was determined by the ratio of the mass of swollen sample to that of the unswollen sample termed swelling ratio. After extraction samples were dried overnight at 100°C and mass determined. The gel content is determined by the ratio of the mass of dried sample to that of the initial sample [7], [8], [9].

3. Results and discussion

3.1. Solid state nuclear magnetic resonance of methyl methacrylate copolymers

As reported in the literature [10], the solid state NMR of the methyl methacrylate shows several characteristic peaks. The first occurs at 177 ppm corresponding to the carbonyl carbon, peaks at 52 and 45 ppm corresponding to the overlap of the quaternary carbon, methine, and methylene carbons, and one at 17 ppm corresponding to the methyl group. Upon examination of the methyl methacrylate/divinylbenzene cross-linked polymers, additional peaks are found at 145 ppm for the quaternary carbons of the divinylbenzene group with another peak at 128 ppm corresponding to the four aromatic protonated carbons. The methine and methylene groups in divinylbenzene overlap the main chain resonance in the methyl methacrylate portion of the copolymer. The percent of divinylbenzene has been calculated using the integration for the carbonyl peak of methyl methacrylate and the quaternary carbon peak of divinylbenzene. Table 1 shows the correspondence between the quantity expected from synthesis and that determined by NMR.

Table 1. Amount of divinylbenzene present by NMR

Expected amount of divinylbenzene (%)	Calculated percent DVB by NMR (%)
10	12
20	22
30	31
40	40

3.2. Gel content and swelling ratio of methyl methacrylate copolymers

The gel content of the methyl methacrylate–divinylbenzene cross-linked polymers indicates that the samples are highly cross-linked (Table 2). Swelling ratios for the methyl methacrylate copolymers are low, indicating a substantial cross-link density for these copolymers. Significantly higher values have been reported for other polymers, such as cross-linked polybutadiene, with a swelling ratio of 4000 [5]. A decrease in swelling ratios is observed as the amount of divinylbenzene is increased which indicates that the cross-links are dependent upon the amount of divinylbenzene present.

Table 2. Gel content (GC) and swelling ratio (SW) of methyl methacrylate–divinylbenzene cross-linked polymers

%DVB	GC (%)	SW (%)	Reaction time (min)
10	83	700	60
20	88	600	60
30	92	400	50
40	91	300	40

3.3. Thermogravimetric analysis of methyl methacrylate copolymers

It has been shown in the literature [11] that poly(methyl methacrylate) degrades in several steps, the first is cleavage of the least stable linkage, which is the head to head linkage occurring at approximately 195°C. (This step is best seen at very low heating rate.) The next degradation step is observed at 270°C and this corresponds to end-initiated depolymerization from unsaturated vinyl ends and the final degradation step observed at 360°C corresponds to random scission initiation [11]. Fig. 1 shows the thermogravimetric analysis curves for the copolymers as well as the virgin poly(methyl methacrylate) in an argon atmosphere. The virgin poly(methyl methacrylate) used in this study begins to decompose at ca. 150°C, probably because of the presence of low molecular weight fractions. Both Fig. 1 and Table 3 show that for the cross-linked copolymers the initial degradation is pushed back and is not as pronounced as for the virgin poly(methyl methacrylate). The onset temperatures of degradation and char formation show an increase as the swelling ratio is decreased and the amount of cross-linking agent is increased.

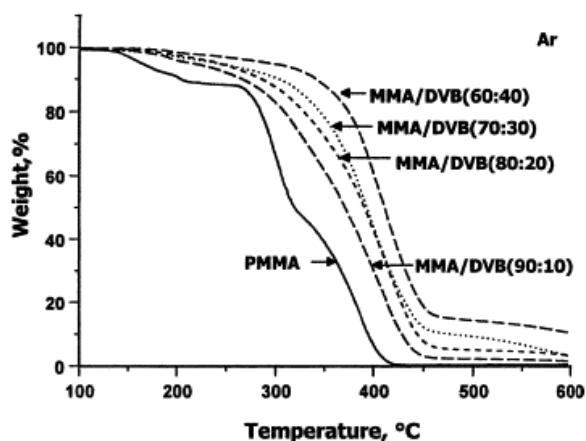


Fig. 1. Thermogravimetric analysis curves for methyl methacrylate–divinylbenzene cross-linked polymers and virgin poly(methyl methacrylate) in argon.

Table 3. Onset temperatures of degradation (5 and 10%) and char formation of methyl methacrylate–divinylbenzene cross-linked polymers

MMA/DVB	Ar			Air		
	$T_{5\%}$ (°C)	$T_{10\%}$ (°C)	Char _{500°C} (%)	$T_{5\%}$ (°C)	$T_{10\%}$ (°C)	Char _{450°C} (%)
PMMA	162	203	0	161	201	0
90:10	214	266	2	202	252	6
80:20	242	285	5	219	273	11
70:30	241	303	9	254	302	19
60:40	294	341	14	256	318	25

3.4. Thermogravimetric analysis/Fourier transform-infrared spectroscopy of methyl methacrylate copolymers

The cross-linked polymer of 60 wt.% methyl methacrylate and 40 wt.% divinylbenzene was analyzed by TGA/FT-IR, Fig. 2, shows a maximum temperature of degradation at 448°C. The initial fragments lost at approximately 280°C contain a carbonyl band at 1748 cm^{-1} and an ether band (C—O—C) at 1173 cm^{-1} indicating that the methyl methacrylate portion is degrading first and the cross-linked portion (divinylbenzene) is still intact [12]. The infrared spectrum at approximately 485°C (Fig. 3) reveals fragments representative of CH aromatic stretch and C=C aromatic stretch corresponding to the loss of the divinylbenzene units. More interestingly fragments representing methyl methacrylate (2970 cm^{-1} CH aliphatic stretch, 1740 cm^{-1} carbonyl stretch, and

1170 cm^{-1} C—O—C stretch) are still evolving at this temperature. Kashiwagi et al. [11] showed that for poly(methyl methacrylate) complete degradation is observed by 450°C, Fig. 3 shows that for the methyl methacrylate-co-divinylbenzene polymer that methyl methacrylate fragments are still present at 485°C indicating that the cross-linking is enhancing the thermal stability of poly(methyl methacrylate) [11].

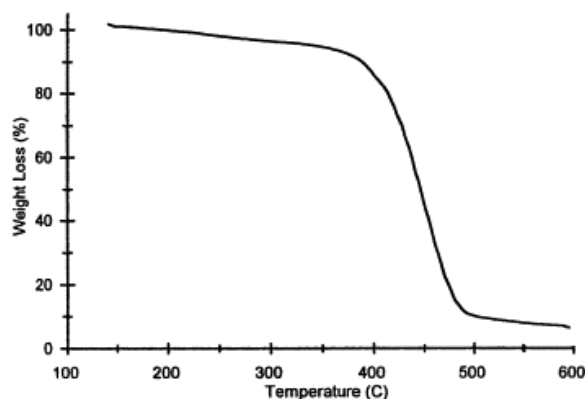


Fig. 2. TGA curve from 60% MMA/40% DVB cross-linked polymer examined by TGA/FT-IR.

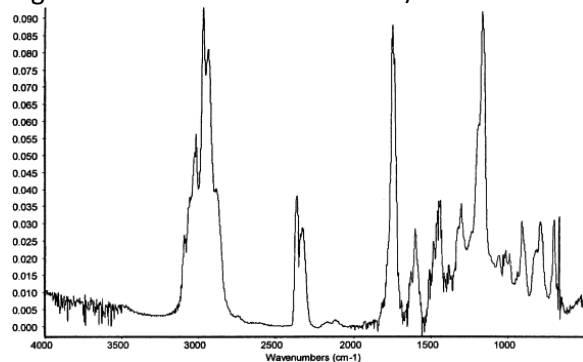


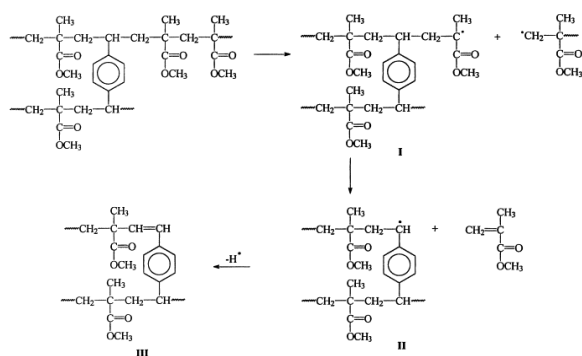
Fig. 3. TGA/FT-IR of 60% MMA/40% DVB cross-linked polymer at 485°C.

3.5. Mechanism of char formation of methyl methacrylate copolymers

Poly(methyl methacrylate) has been shown to degrade by an unzipping radical chain reaction without chain transfer to give monomer [13], [14], [15], [16], [17]. Initiation typically occurs at the unsaturated chain ends or at weak links in the polymer chain. The onset of degradation for cross-linked polymers are higher than that of the virgin poly(methyl methacrylate).

It has been shown that as the swelling ratios decrease the onset temperatures of degradation are increasing. This phenomenon can be considered to be an indication that the number of cross-links control the degradation and this leads to the conclusion that as the amount of divinylbenzene is increased, both the onset temperatures of degradation and char formation increase.

Initially the copolymer degrades as virgin poly(methyl methacrylate), producing a tertiary radical which is capable of depropagation to form monomer (Scheme 1). Once the cross-links are reached degradation is stopped because the benzene ring deactivates (stabilizes) radical II and further stabilization is achieved by hydrogen abstraction from methylene groups. The new double bond (III) could participate in new cross-linking reactions at higher temperatures, increasing the fraction of non-volatile residue.



Scheme 1. Degradation sequence for poly(methyl methacrylate) cross-linked with divinylbenzene.

It has been previously shown that methyl methacrylate cross-linked with dimethacrylates shows no enhancement in the thermal stability of methyl methacrylate [6]. Therefore, the aromatic nature of divinylbenzene must be the reason for the enhancement in this study.

3.6. Gel content and swelling ratio for styrene copolymers

The structures of the cross-linking agents can be seen in Fig. 4, of these cross-linking agents only the bisphenol A dimethacrylate has aromatic character while the other three are all aliphatic in nature.

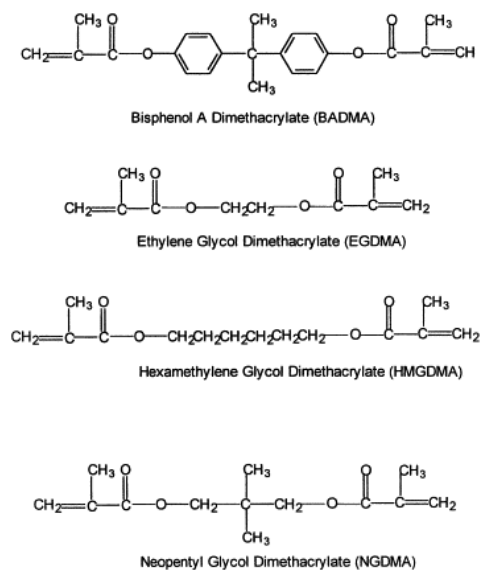


Fig. 4. Structures of cross-linking agents.

3.7. Solid state nuclear magnetic resonance of styrene copolymers

Solid state NMR of polystyrene shows three prominent peaks [10]. The first is at 41 ppm corresponding to overlap of the methine and methylene carbons. Two aromatic carbon peaks are observed, one at 128 ppm, attributable to the protonated carbons, and the other at 146 ppm, corresponding to the non-protonated carbons. The spectra of the copolymers show the presence of the dimethacrylate units. Using the quaternary carbon of the styrene and the carbonyl group (approximately 176 ppm) of the various dimethacrylates, the percent incorporation of dimethacrylates can be determined and compared to the synthetic ratios (Table 4), the agreement is quite good.

Table 4. Amount of dimethacrylate incorporated into cross-linked polymers

Expected amount of dimethacrylate (%)	Calculated amount from NMR (%)
---------------------------------------	--------------------------------

NGDMA	
20	16
30	30
40	37
HMDMA	
10	14
20	23
30	29
40	39
EGDMA	
10	15
20	25
30	32
40	44
BADMA	
10	29
20	30
30	30
40	40

The gel content of the styrene-co-dimethacrylate polymers indicates that the polymers have substantial cross-link density Table 5. This is further shown by a slight decrease in swelling ratio as the amount of cross-linking agent is increased. Again, this indicates that the cross-link density is dependent upon the amount of dimethacrylate present.

Table 5. Gel content and swelling ratios for styrene-dimethacrylate cross-linked samples

% Dimethacrylate	GC (%)	SW (%)	Reaction time (h)
BADMA			
10	96	400	5
20	85	400	3
30	91	300	2
40	82	300	1.5
HGDMA			
10	84	600	15
20	94	400	7
30	94	300	3
40	99	300	2.5
EGDMA			
10	84	700	28
20	78	700	12
30	95	300	9
40	94	300	2.75
NGDMA			
10	NO	GEL	
20	77	700	24
30	82	600	9
40	86	500	6.5

3.8. Thermal analysis of styrene copolymers

Table 6 shows the onset temperatures of degradation and char formation for the styrene–co-dimethacrylate polymers and the virgin polystyrene, there is no overall increase in the initial temperature of degradation of these copolymers. On the other hand all cross-linked copolymers decompose slower than virgin polystyrene and show some thermal stabilization as the degradation proceeds. Only the styrene–co-bisphenol A dimethacrylate polymers show a significant increase in the onset temperatures of degradation and in char formation and the TGA curves are shown in Fig. 5. For the purpose of comparison, the TGA curve of the styrene–ethylene glycol dimethacrylate copolymer is shown in Fig. 6. It is clear that the onset temperature of the degradation is lower for the copolymer but, at 30–40% degradation, the copolymers are more thermally stable than virgin polystyrene.

Table 6. Onset temperature of degradation and char formation for styrene–dimethacrylate cross-linked polymer and virgin polystyrene

	Ar			Air		
St/	$T_{5\%}$ (°C)	$T_{10\%}$ (°C)	Char _{500°C} , %	$T_{5\%}$ (°C)	$T_{10\%}$ (°C)	Char _{450°C} , %
EGDMA						
PS	297	322	2	288	314	2
90:10	208	298	2	205	292	3
80:20	233	307	1	216	289	3
70:30	252	309	1	239	296	3
60:40	251	304	2	256	298	5
NGDMA						
PS	297	322	2	288	314	2
80:20	240	292	1	240	293	3
70:30	248	306	2	234	296	2
60:40	243	300	2	252	293	4
HMGDMA						
PS	297	322	2	288	314	2
90:10	204	300	0	210	297	3
80:20	217	301	1	208	289	3
70:30	220	301	2	225	293	4
60:40	237	302	3	226	290	5
BADMA						
PS	297	322	2	288	314	2
90:10	235	327	2	214	307	5
80:20	240	330	3	225	306	5
70:30	255	331	5	238	316	15
60:40	276	338	9	262	328	18

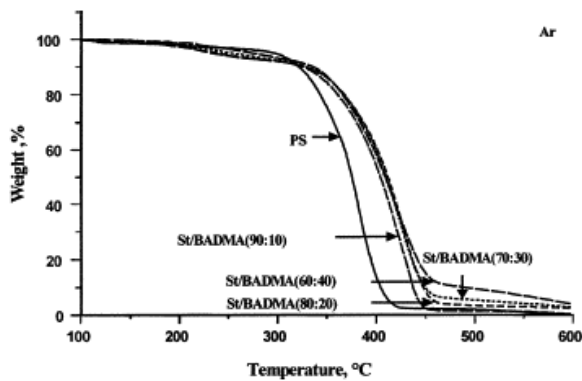


Fig. 5. Thermogravimetric analysis of styrene–dimethacrylate crosslinked samples.

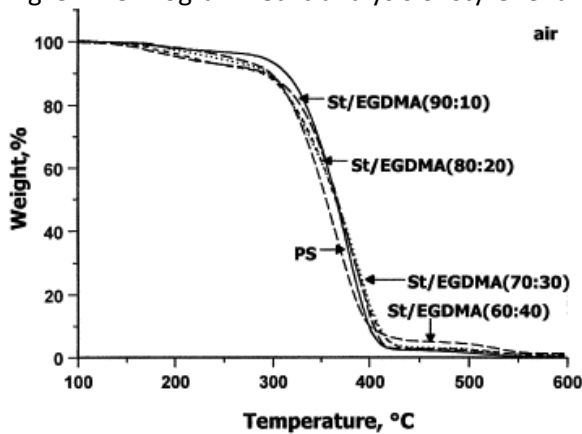


Fig. 6. TGA curves for styrene–ethylene glycol dimethacrylate copolymers.

3.9. Thermogravimetric analysis/Fourier transform-infrared spectroscopy of styrene copolymers

A copolymer of styrene (60%) and bisphenol A dimethacrylate (40%) was prepared and characterized by thermogravimetric analysis coupled with Fourier transform-infrared spectroscopy. During the initial degradation, approximately 180°C, a spectrum containing peaks representative of aromatic rings is observed, indicating that the polystyrene portion is degrading while the cross-links remain intact. Above 460°C peaks corresponding to aromatics, along with a peak at 1740 cm^{-1} , characteristic for the carbonyl ($\text{C}=\text{O}$), and at 1140 cm^{-1} , C—O—C stretch characteristic of esters (Fig. 7), are observed together with peaks at 1508 and 910 cm^{-1} representative of a 1,4-substituted ring [12]. These peaks are indicative of cleavage of the cross-links and the evolution of bisphenol A dimethacrylate. The infrared spectra indicate that the polystyrene portion of the cross-linked polymers undergoes initial degradation, leaving the cross-linked portions still intact. The degradation of the cross-linked regions eventually occurs at higher temperatures.

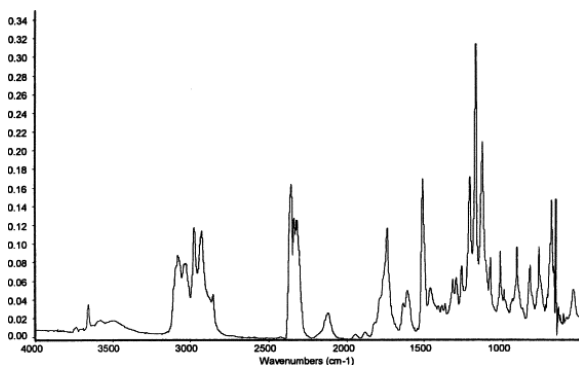
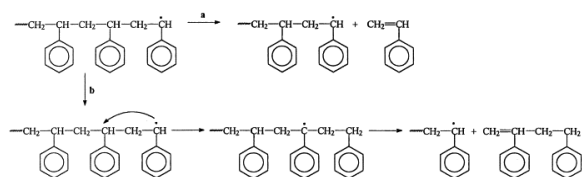


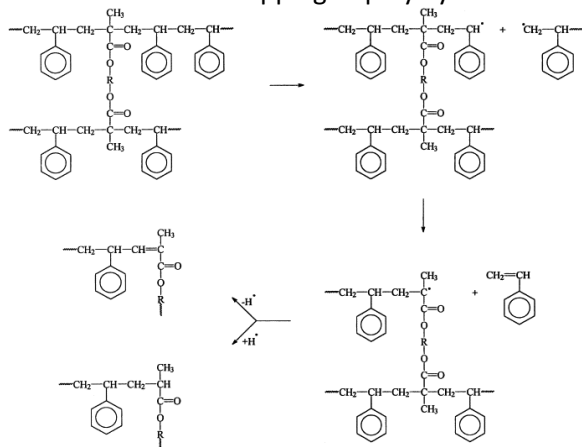
Fig. 7. IR of gases evolved at 459°C of 60% styrene/40% bisphenol A dimethacrylate cross-linked polymer.

3.10. Mechanism of char formation

Degradation of polystyrene has been studied extensively, the degradation begins at the weak links and proceeds by random scission with hydrogen transfer to give both monomer and oligomer (Scheme 2) [6], [13], [18]. Since both the monomer and oligomer will volatilize easily neither contribute to char formation. In the degradation process of a cross-linked polystyrene once the depropagation process reaches a cross-link it would be necessary to break two bonds to release the cross-link (dimethacrylate). But, the depropagation of the two polystyrene chains is occurring at different rates while the radical in one chain can stay in the "cage" with the double bond or creation of a double bond in the chain can occur by hydrogen abstraction leading to stabilization of the chain (Scheme 3).



Scheme 2. Chain unzipping of polystyrene — monomer and oligomers.



Scheme 3. Possible modes of degradation for styrene cross-linked with dimethacrylates leading to enhancement of char formation.

4. Conclusions

For the methyl methacrylate-co-divinylbenzene polymers an increase in onset temperature of degradation and char formation is observed as the amount of divinylbenzene is increased. It has been shown that the cross-link density increases as the amount of divinylbenzene incorporation is increased, resulting in a reduced tendency for the cross-linked polymers to undergo degradation. It can be inferred that this enhancement is due to the aromatic nature of the divinylbenzene.

The styrene-co-dimethacrylate polymers show onset temperatures of degradation that are lower in all cases. An enhancement in thermal stability at higher temperatures is observed, especially in the case of bisphenol A dimethacrylate. Overall the cross-link density correlates to the amount of dimethacrylate present. All of the cross-linked samples result in char formation, though not as pronounced as the MMA-co-DVB polymers. An increase in char formation and enhanced thermal stability is observed in the case of the bisphenol A dimethacrylate cross-linked polystyrene, again suggesting that the aromatic character of the cross-links is

responsible for the char formation. These results would lead to the conclusion that even though cross-link density is high, it is the type of cross-link not the number of cross-links that determine char formation.

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