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Copolymerization of Maleic Anhydride with Styrene and α-Olefins. Molecular and Thermal Characterization

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Copolymers of styrene-maleic anhydride, SMA, and maleic anhydride-α-olefins (1-hexene, 1-octene, 1-decene, 1-dodecene, 1-tetradecene and 1-hexadecene) have been synthesized by free radical polymerization, using azobisisobutironitrile and benzoyl peroxide as initiators. Copolymers were characterized by gel permeation chromatography, viscosity measurements, FT-IR, differential scanning calorimetry (DSC) and thermal gravimetry analysis (TGA). The copolymers of maleic anhydride-α-olefins exhibit a monomodal molecular weight distribution. During the TGA analysis, decomposition of maleic anhydride and α-olefins was observed by FT-IR. Carboxylic acids and gaseous CO_2 *were identified as decomposition products of the copolymers close to 200°C. The SMA copolymer was esterified with 2-propanol, sec-butanol and tert-butanol at 65°C using 4-dimethylaminopyridine catalyst and tetrahydrofurane solvent. The rate of reaction and limiting ester yields are lower than those obtained in the esterification with primary alcohols.*

Keywords copolymerization, glass transition, styrene-maleic anhydride, styrene-olefin, thermal degradation

Introduction

Copolymers of styrene and maleic anhydride, commercially produced as SMA resins, are known to show a strong tendency towards alternation, when they are prepared under moderate temperature conditions (1–5). The degree of hydrophilicity and other properties of the copolymers may be modulated through a wide range of chemical modifications such as reactions with alcohols (6, 7), amines (8, 9) and alkalis (10), giving numerous useful derivatives (11). For example, esterification and imidation of the MA function have been used to form anionic, cationic and nonionic alkyl derivatives which exhibit surfactant properties (12). Different charged derivatives of SMA have also been used as dispersants

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in colloidal applications (13). These copolymers, containing carboxylic acid groups, are anionic, cationic, Zwitterionic, or nonionic surfactants depending on the pH value. Hu and Lindt (14) showed that the kinetics and thermodynamics of the mono esterification of SMA with alkyl alcohols is independent of the alkyl chain length. Recently, we have reported a study on the esterification of SMA copolymers with primary alcohols (methyl, n-propyl, n-butyl, n-hexyl, n-octyl and n-decyl alcohol), where the degree of esterification, molar mass (GPC) and glass transition temperatures (Tg) were determined (15).

On the other hand, copolymers of MA with olefins have also been extensively studied, and a large number of patents (3–5) has been registered. Most of them are mainly concerned with the ethylene copolymer (EMA), which has very useful properties as thickeners, stabilizers, suspending agents and so forth, for detergents applications (16). In general, it is known that lower olefins react more easily with MA than higher olefins, producing alternating copolymers. For higher olefins, such as 1-hexene and 1-octene, it has been found that copolymerization with MA produces only low-molecular-weight copolymers in low yields (17). It has also been shown that the potassium salts of these copolymers form hydrophobic microdomains, exhibiting behavior analogue to micelles (18, 19). Therefore, in the present paper we report the results obtained in the study of the copolymerization of maleic anhydride with long-chain α-olefins (C_6–C_{16}). The thermal behavior and molar mass of the obtained copolymers are examined as a function of the olefin length.

In addition, we have extended our previous study on the esterification of SMA by using secondary alcohols, to compare the kinetic behavior of lineal and branched alcohols in this reaction.

Experimental

Materials

Maleic anhydride (MA) and 4-(dimethylamino)pyridine (DMAP) were supplied by Aldrich. Styrene and azobisisobutironitrile (AIBN) were obtained from Fluka A.G. Aliphatic alcohols and α-olefins were purchased from Merck. Tetrahydrofurane, THF, was dried and distilled over sodium immediately before use. All others chemicals were used as received.

Copolymerization of Styrene and Maleic Anhydride (SMA) (1–5)

MA (0.069 moles), styrene (0.022 moles) and AIBN (1.1 mmol) were added to a mixture of acetone (12 mL) and toluene (60 mL). The mixture was magnetically stirred until a homogenous and transparent solution was formed. Then, the reaction mixture was deaerated by a freeze-thaw cycle under high-vacuum conditions, filled with argon and immersed in a thermoregulated bath at 60°C for 40 min. The polymerization is evidenced by formation of a milky white precipitate. The solvent was evaporated in a rotary evaporator, and the copolymer was redissolved in dry THF (65 mL), obtaining a viscous and transparent solution. This solution was poured over 200 mL of hexane; the copolymer (precipitated in a white spangle form) was collected by filtration, and vacuum dried at 70°C for 6 h. The conversion was 40%.

Copolymerization of α-Olefins and Maleic Anhydride (1–5)

The copolymerization of α-olefins and MA were carried out by following a procedure similar to that described for the synthesis of SMA copolymers. MA (0.017 moles), benzoyl peroxide (4.05 mmol), and the respective olefin (0.0204 mol) were added to a mixture of toluene (20 mL) and acetone (4 mL). The olefins used were 1-hexene, 1-octene, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene. The mixture was deaerated, filled with argon, and reacted at 70°C during 12 h. After solvent evaporation, the product was dissolved in toluene (app. 7 mL) to separate all unreacted maleic anhydride, since this compound is insoluble in toluene. The polymer solution was then precipitated from hexane (75 mL), obtaining a very fine white powder. The product was finally filtered, and dried for 6 h, under reduced pressure at temperatures ranging between 30-50°C, depending on each olefin. The yields were near to 15% for all olefins, except 1-hexene which was 30%.

Esterification of SMA Copolymer with Primary and Secondary Alcohols

The SMA copolymer (0.01 mol, on a molar repeat unit basis), and DMAP (0.41 mol) were dissolved in 60 mL of THF. The reaction mixture was magnetically stirred until a transparent and homogenous solution was obtained. Then, the needed amount of alcohol was added (0.08 mol). The flask was attached to a reflux system and immersed in a thermoregulated bath at 65°C with constant agitation. The degree of esterification was monitored as a function of time by taking samples at regular intervals. These samples were precipitated from 25 mL of hexane, filtered, and vacuum dried at 60°C for 8 h, until total solvent extraction.

Results and Discussion

The molecular weight M_v of poly(styrene-co-maleic anhydride), SMA, was determined by measurements of intrinsic viscosities, and by using the Mark-Houwink relationship:

$$[\eta] = k \times M_v^a$$

where $k = 5.07 \times 10^{-5}$ and $a = 0.81$ in THF (20). On the other hand, M_w values were obtained by GPC, using a polystyrene calibration curve. The results obtained for two different samples (Table 1) show that M_v is much higher than M_w, probably due to differences in polydispersity, (IP = 2.55).

The SMA copolymer was esterified with linear and branched aliphatic alcohols in order to compare the kinetic behavior of different alcohols in this reaction (14). The degree of reaction is defined as the ratio of the concentration of maleic anhydride

Table 1
Intrinsic viscosity (THF), molecular weight, and polydispersity (IP) of synthesized SMA copolymers

Sample	$[\eta]$ dl/g	Mv (g/mol)	IP
SMA 1	0.7002	129200	2.58
SMA 2	0.6800	124600	2.55

groups reacted over the concentration of total repeat units (21), determined by FT-IR, by using the peaks at 1720 and 1649 cm^{-1}, corresponding to the appearance of the ester carbonyl, and the peaks at 1852 and 1780 cm^{-1}, corresponding to the maleic anhydride disappearance.

Table 2 shows the limiting percentage of ester obtained in the esterification reaction of MA with 2-propanol, sec-butanol and tert-butanol. Also, for comparison is included the values found previously for linear alcohols. From this data, it is clear that the extent of reaction depends on the nature of the alcohol. For example, for 2-propanol the reaction reach a 52% of conversion after 24 h of reaction, while for sec-butanol and tert-butanol the limiting percentage of ester are 37% and 11%, respectively, after 24 h of reaction. These results suggest that the esterification rate is determined by a steric effect that limits the accessibility of the alcohol towards the complex formed by the anhydride group and the catalyst (DMAP). This effect is more evident if we compare the results obtained for the reaction of primary linear alcohols, such as 1-propanol, 1-butanol, and 1-hexanol (see Table 2), under the same temperature, solvent and catalyst conditions. For these alcohols, the extent of reaction increases with increasing length of alkyl chain and then remains constant around 70%. Similar results have been reported by Hu and Lindt (14), who found that the esterification of MA with 1-octanol and 1-hexadecanol does not depends on the length of the alkyl chain.

The copolymers obtained by esterification with branched alcohols were analyzed by DSC, and the results are presented in Table 3. The thermograms show three peaks between 90°C and 250°C; except for the copolymer reacted with tert-butanol which did not displayed the peak at 90°C. The peak 3 corresponds to the glass transition temperature (Tg) of the copolymers. The three Tg values are very similar and they compare quite well with those obtained for n-propanol and n-butanol, 250 and 239°C respectively, suggesting that the branching of the alcohol chain does not affect the Tg. In other words, Tg is determined exclusively by the number of carbon atoms in the side alkyl chain. It has been found previously, that copolymers esterified with longer primary alcohol exhibit a much lower Tg, i.e., 144°C and 136°C for n-octanol and n-decanol (15), respectively.

Polymerization of α-Olefins And Maleic Anhydride

The intrinsic viscosities, molecular weight and yield of the different copolymers of maleic anhydride and olefins (C_6–C_{16}) are given in Table 4. For comparison, a commercial sample of MA-1-octadecene has also been included.

Table 2

Degree of esterification of SMA copolymer by branched and linear alcohols after 24 h of reaction

Alcohol	Conversion, %	Alcohol	Conversion, %
2-propanol	52	Metanol	54
sec-butanol	37	n-propanol	60
tert-butanol	11	n-butanol	70
		n-hexanol	68

Table 3
Differential scanning analysis of SMA copolymers esterified with branched alcohols

Alcohol	Peak 1 (°C)	Peak 2 (°C)	Peak 3 (°C)
2-propanol	90.50	181.40	249.25
sec-butanol	89.40	176.80	250.10
tert-butanol	—	177.25	249.03

Table 4
Intrinsic viscosities and molecular weights (GPC) of MA/α-olefins (C_6–C_{16}) copolymers

Copolymer	[η]	Mw	Mn	IP	Yield (%)
MA/1-Hexene	0.0241	3750	2800	1.33	30
MA/1-Octene	0.0423	7300	5300	1.38	13
MA/1-Decene	0.0591	11500	5600	2.05	15
MA/1-Dodecene	0.0476	10700	7300	1.46	18
MA/1-Tetradecene	0.0216	5100	3500	1.46	15
MA/1-Hexadecene	0.0122	7900	5300	1.49	11
MA/1-Octadecene[a]	0.1281	29600	12000	2.47	—

[a] Commercial sample, Aldrich Ltd.

The molecular weight number average of the copolymers ranges between 2,300 and 12,000, approximately, and there is not a clear dependence of Mw on the olefin nature. However, a decrease of the copolymerization yield with increasing length of the alkyl olefin chain is observed.

The polydispersity values are between 1.33 and 2.04, which are characteristic of free radical polymerizations. In addition, the GPC chromatograms displayed a mono disperse distribution, (Figure 1), which indicates a single type of chain growth. By considering the values of Mn and Mw obtained by GPC, it is possible to obtain an estimate of the average number of repetitive units in the linear copolymer chain. Considering the molecular weight of the repetitive unit, which varies for each olefin, the average number of these units by polymer chain oscillates between 12–27 for the studied copolymer set. For example, the chain of the alternating MA/1-decene copolymer contains 23 repetitive units, each of them formed by one maleic anhydride group and one alkyl chain with ten carbon atoms.

On the other hand, the effect of initiator concentration on the yield and molecular weight was also studied. The results indicate that the maximum yield and higher molecular weights are obtained with a concentration of benzoyl peroxide equal to 4.09×10^{-4} M.

In the following section the thermal behavior of some copolymers are analyzed. The TGA thermograms of the MA/1-octene and MA/1-hexadecene copolymers are shown in Figures 4 and 5, respectively. These analyses were carried out in a TGA–FT-IR coupled instrument, which allows simultaneously study of the thermal behavior and to record the FT-IR spectra of the decomposition products. Regarding the thermal stability of the

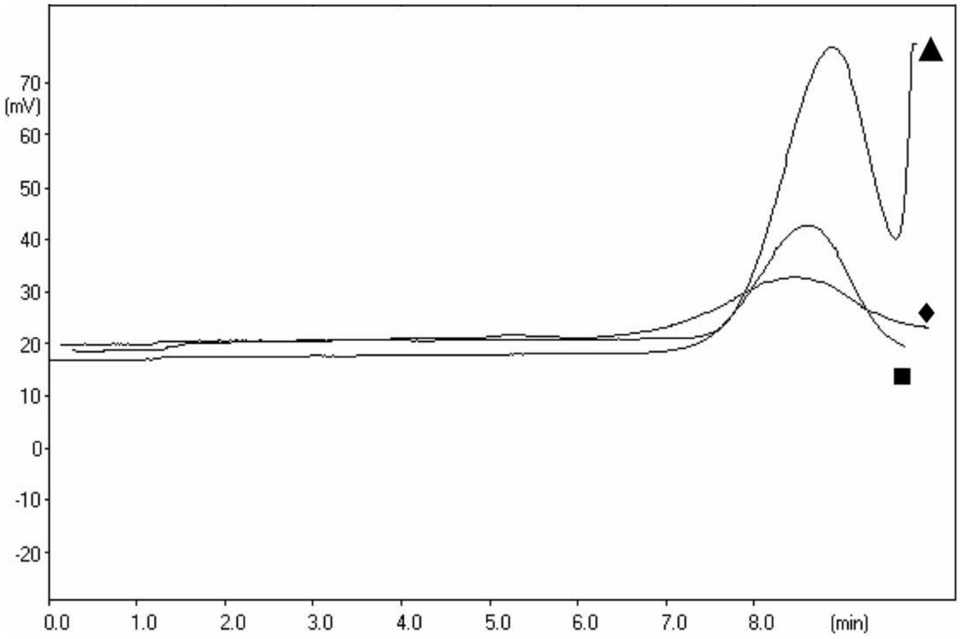

Figure 1. Chromatogram of copolymers MA/1-hexene(▲), MA/1-decene (■), MA/1-dodecene(◆) (solvent mixture acetone-toluene).

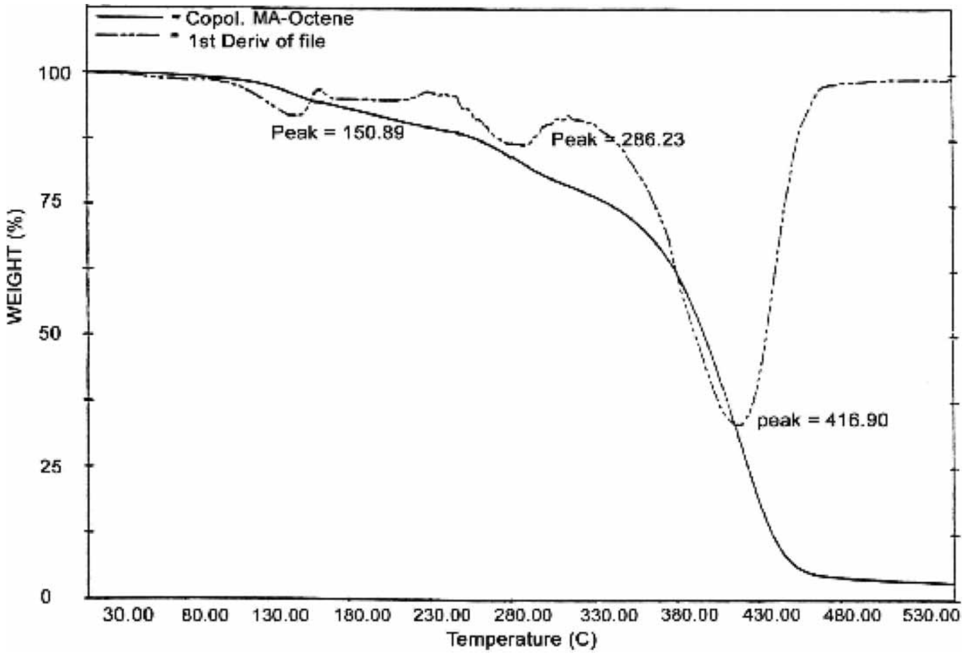

Figure 2. TGA analysis of maleic anhydride-1-octene copolymer.

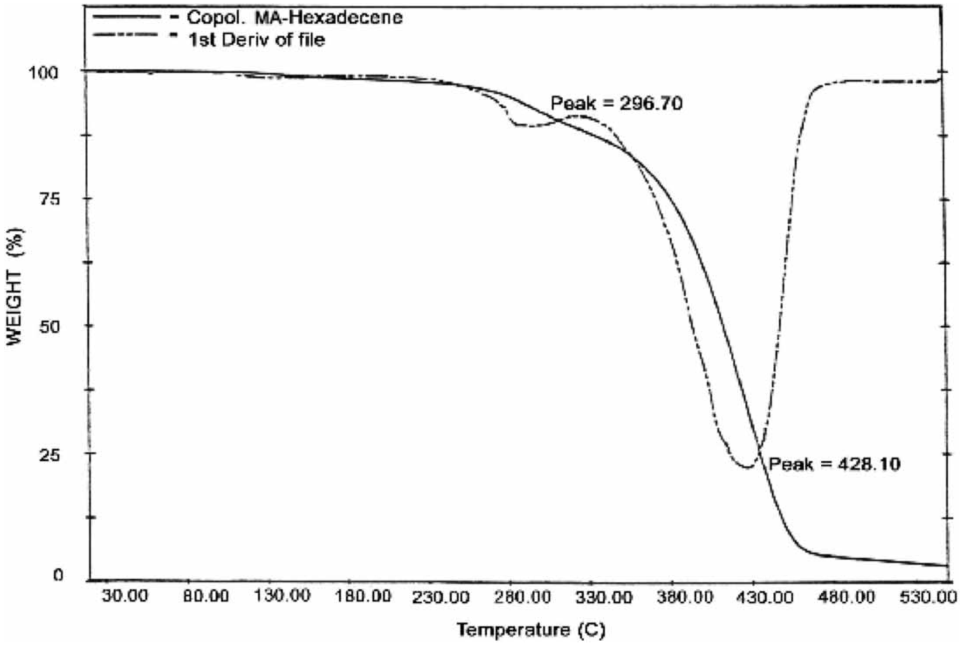

Figure 3. TGA analysis of maleic anhydride-1-hexadecene copolymer.

analyzed copolymers and their decomposition products, the thermogram of AM/1-octene copolymer shows a first peak at 150°C, with no apparent loss of mass (Figure 2). This peak is not observed in Figure 3 for the MA/1-hexadecene. Additionally, both copolymers displayed a peak around 290°C (286.2°C and 296°C for MA/1-octene and

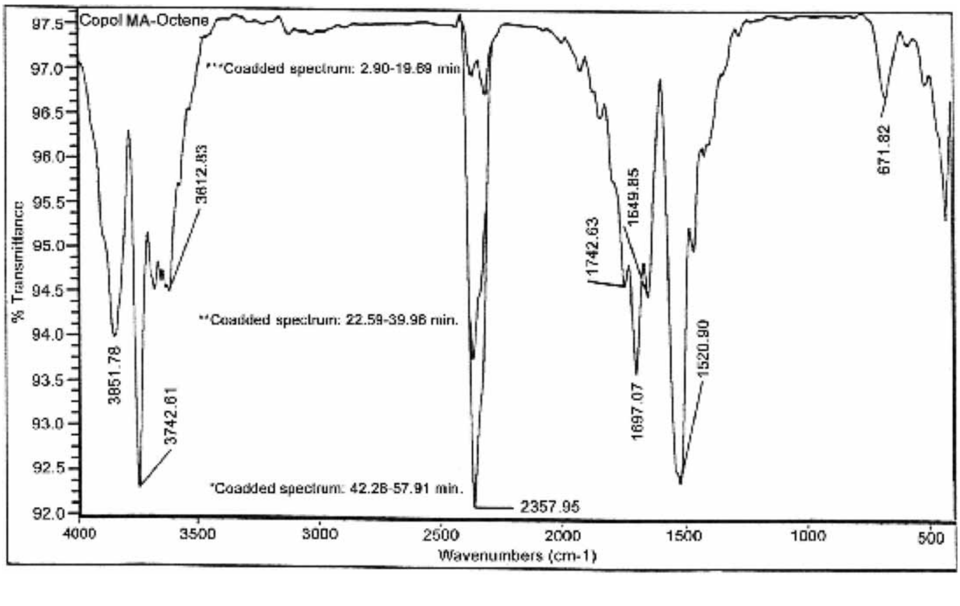

Figure 4. FT-IR of TGA decomposition products of maleic anhydride-1-octene copolymer.

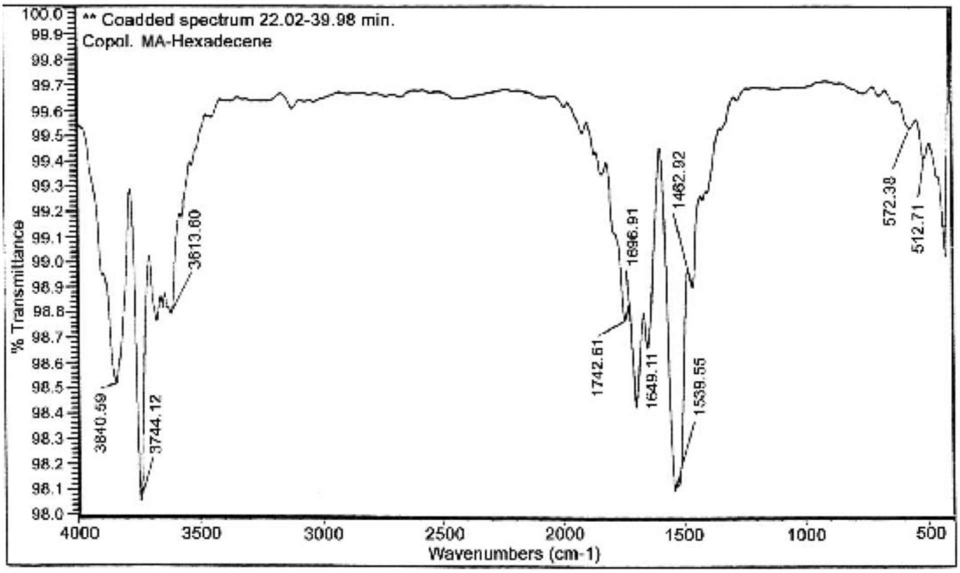

Figure 5. FT-IR of TGA decomposition products of maleic anhydride-1-hexadecene copolymer.

MA/1-hexadecene, respectively). Around 420°C, both copolymers decompose almost completely, with more than 90% mass loss, but the MA/1-hexadecene copolymer exhibits a decomposition temperature 10°C higher than that observed for MA/1-octene. When comparing, the co added FT-IR of decomposition products from both copolymers, Figures 4 and 5, interesting information can be drawn. The displayed spectra correspond to accumulated fractions at different temperatures from decomposition products, which are shown in the respective spectra. Figure 4 for instance, the MA/1-octene copolymer shows sharp peaks in the region of the 3600–3800 cm^{-1}, corresponding to non-associated -OH vibration absorptions, along with the absorptions at 1697 and 1742 cm^{-1}, which correspond to a C=O group. These vibrations would possibly correspond to decomposition of the carboxylic acid functionality.

The FT-IR obtained from the decomposition products of MA/1-octene (Figure 4) shows a sharp absorption at 2357 cm^{-1}, which increases with increasing time. The three growing absorptions displayed in the range approximated of 3 up to 58 min, correspond to the heating speed of the sample at the following temperatures;

$$2.9-20 \text{ min} \sim 30-200^{\circ}\text{C}$$
$$22-40 \text{ min} \sim 220-400^{\circ}\text{C}$$
$$42-58 \text{ min} \sim 420-580^{\circ}\text{C}$$

This absorption is assigned to gaseous CO_2 (22), which is originated from maleic anhydride decomposition. This peak is not observed in the case of MA/1-hexadecene copolymer, Figure 5. The MA/1-octene copolymer would be less stable than the MA/1-hexadecene. In other words, the longer alkyl side chain (1-hexadecene) would probably be protecting the maleic residue. In this way, this group would be less exposed to the thermal decomposition as compared with the MA/1-octene copolymer. It must be considered that the molecular weight for these copolymers is almost identical, as shown in Table 3.

Thermal study of the SMA copolymer showed that the starting point of decomposition is around 200°C, with the main products identified by chromatography and mass spectrometry as toluene, ethylbenzene, 1,3-diphenylpropane, 3-phenyl-2-hexenone, 3-phenylbutyric acid, CO_2 and water (23). In addition, we have detected more than fifteen volatile compounds in the pyrolysis of the SMA copolymer.

As we observed, for the studied MA-olefins copolymers, significant decomposition appears at ca. 290°C, so these copolymers would exhibit a higher thermal stability than the SMA copolymer when comparing higher side chain olefin and similar molecular weight.

Conclusions

Maleic anhydride-styrene copolymers esterified with secondary and tertiary alcohols, show that the esterification kinetic is slower than that observed with primary alcohols. The conversion for secondary alcohols does not exceed 52%, even up to 26 h of reaction, well below those of equal carbon number with primary alcohol groups. The Tg of copolymers esterified with 2-propanol, sec-butanol and tert-butanol, are comparable with those of primary alcohol of equal number of carbons.

Copolymerization of long-chain olefins with maleic anhydride in the system acetone-toluene/benzoyl peroxide, gave copolymers with molecular weights in the range of 3700–11,500 g/mol. The olefins having the longest alkyl chain produce copolymers with the highest molecular-weight polymers, in a yield of 15%. The distribution of molecular weights is mono modal; therefore, secondary events in the growth of the chain do not exist. It was not possible to observe Tg in these copolymers. During thermal decomposition, in copolymers of shorter side chains, carboxylic acids products are obtained. The maleic anhydride copolymer is decomposed by freeing gaseous CO_2.

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