SYNTHESIS AND CHARACTERIZATION OF ETHYL ACRYLATE-METHYL ACRYLATE OLIGOMERS WITH A HYDROXYL END GROUP

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A study on the method for the preparation of monohydroxyl functionalized oligomers has been performed using ethyl acrylate and methyl acrylate together with 2'2' Azobisisobutyronitrile-AIBN (initiator), and 2-mercaptoethanol (2-MEOH) as functional chain-transfer agent. The estimation of the kinetics of the free radical chain polymerization by using statistical techniques is supported by the experimental studies. The oligomers compositions were determined by a quantitative analytical IR spectroscopic technique.

INTRODUCTION

Functional chain-transfer agents are useful for preparing single hydroxyl-terminated polymethacrylates oligomers [1−2] and have potential for a wide range of applications because of the presence of hydroxyl functional groups at the chain end, which provide sites for chemical modification, which in turn can affect the physical properties of the resulting polymers [3]. The use of oligomers that contain only a hydroxyl group on the end is extensive and star-shaped, grafted, and comb-like polymers with regular spacings can be produced in this way. In the preparation process of macromonomers, copolymers with comb-shaped structure are utilized, and the chemical parameters are very important in determining the branch distribution in the resulting comb-shape copolymers [4−5]. In general, this issue is of tremendous relevance for the production of low molecular mass acrylic oligomers, used in several applications, ranging from adhesives to high solid-content elastomers [6−7].

Accordingly, this study represents an effort to add to the existent knowledge of stereochemically designed macromolecules, in particular by using poly(ethyl acrylate) (PEA) and poly(methyl acrylate) (PMA) oligomers. In particular, in this work a statistical experimental design approach (2^2 fractional factorials) was employed to determine how different reaction parameters may influence the conversion and the molecular mass distribution, during the synthesis by batch solution polymerization in the presence of a chain transfer agent (2-MEOH). The poly(ethyl acrylate) (HTPEA) and poly(methyl acrylate) (HTPMA) single hydroxyl-terminated oligomers were characterized and evaluated by Gel Permeation Chromatography (GPC), Infrared spectroscopy (IR), UV-VIS spectroscopy, Raman microscopy (RS), and Differential Scanning Calorimetry (DSC).

In the present work, oligomers were prepared by the chemical reaction of acrylic monomers as shown schematically in Figure 1. For comparison, polyacrylates with no chemical modification whatsoever (PAE and PAM) were prepared in the absence of 2-MEOH.

EXPERIMENTAL

Materials

Ethyl acrylate (EA), Methyl acrylate (MA), 2-Mercaptoethanol (2-MEOH), 2′2′ Azobisisobutyronitrile (AIBN), Pyromellitic dianhydride (PMDA), Neopentyl glycol (NPG), 1,4 butanediol (1−4 BD), and
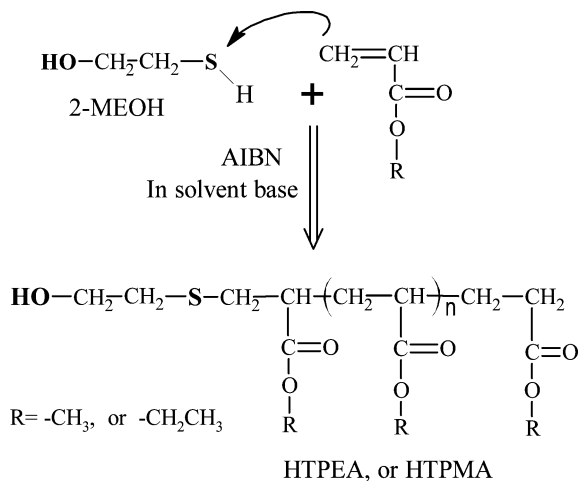
FIGURE 1 Structures of the single hydroxyl-terminated polyacrylate oligomers studied in this work.

thymol blue were purchased from Aldrich. N′N-Dimethyl formamide (DMF) and Imidazole (IMDA) were obtained from Sigma.

Purification of Reagents

Ethyl acrylate and Methyl acrylate were washed twice with 5% NaOH to remove polymerization inhibitor, then twice with $NaHCO_3$, and finally, twice with distilled H_2O. After drying over $MgSO_4$, the samples were distilled under partial vacuum and under a nitrogen atmosphere.

The initiator, AIBN, was recrystallized twice from methanol. The chain transfer agent, 2-MEOH, 1−4 BD, NPG, DMF, and IMDA were used without further purification. The pyromellitic dianhydride was heated at 160°C for 24 h before being used. The solvents toluene, hexane, and chloroform were refluxed and distilled under partial vacuum under nitrogen atmosphere.

Synthesis Route

The polymerization experiments were carried out in a previously flamed borosilicate reaction flask equipped with a magnetic stirring bar, using toluene as solvent. The initiator, monomer, and transfer agent were weighed and then added continuously during 6 min into the flask containing refluxing toluene in a nitrogen atmosphere. A relatively high concentration of initiator and of 2-MEOH was used for

TABLE 1 Reagent Concentrations and Reaction Conditions of the 2^2 Factorial Design used in the HTPEA and HTPMA Polymerization

Runs		Mole ratios, AIBN/Monomers/2-MEOH	Temperature $^\circ$C	Time hrs
HTPEA-1/1	HTPMA-1/1	2/1000/100	55	3.0
HTPEA-1/2	HTPMA-1/2	1/1000/100	65	1.5
HTPEA-1/3	HTPMA-1/3	2/800/100	65	3.0
HTPEA-1/4	HTPMA-1/4	1/800/100	55	1.5
HTPEA-1/5	HTPMA-1/5	2/1000/50	55	1.5
HTPEA-1/6	HTPMA-1/6	1/1000/50	65	3.0
HTPEA-1/7	HTPMA-1/7	2/800/50	65	1.5
HTPEA-1/8	HTPMA-1/8	1/800/50	55	3.0

the purpose of guaranteeing a low molecular weight. The reaction temperature and time were chosen from a practical point of view because the acrylates have a very high reactivity [8−9]. Polymerization reactions were run at constant temperature of 55° or 65°C in a thermostated oil bath.

Purified polymers were obtained by dissolving the product in toluene, precipitating it into a large excess of n-hexane, then redissolving in chloroform. After drying at room temperature in a vacuum desiccator for several hours, the products were heated in a vacuum oven at $55 \pm 2^\circ$C. The obtained polymers were clear, transparent, and extremely tacky.

Based on a 2^2 factorial statistical design, 5 factors were employed to estimate their level of statistical significance on both the conversion and the molecular weight. All data for synthesis of HTPEA and HTPMA with different ratios of 2-MEOH and AIBN are summarized in Table 1.

Characterization Techniques

The molecular weight distribution was determined by gel permeation chromatography (GPC). A polystyrene gel column from Polymer Ultrastyragel (HR6, HR5, HR4, HR3, and HR1) and THF as eluent were used. Polystyrene standards from Polymer Laboratories were used for calibration.

The isolated hydroxyl-terminated PEA and PMA were analyzed for conversion by gravimetry in the form of percent monomer converted to polymer on a mass basis.

The nature and extent of specific interactions of five main factors upon conversion were studied by using the analysis of variance of

Fisher and the Student *t*-test to demonstrate the statistical significance of the studied factors, using the commercial statistical package "Statgraphics" [10].

Hydroxyl number of polymers HTPEA and HTPMA were determined by the pyromellitic dianhydride method. The pyromellitic dianhydride was heated at 160°C for 24 h before being used [11]. The amount of sample utilized was 3.0 g based on the weight and the anticipated hydroxyl value of the polymer [12−13]. The titration method used PMDA in DMF with IMDA as the catalyst and thymol blue as indicator [14−16]. The method was checked with 1−4 DB (99+% pure) and NPG (99+% pure).

Infrared spectroscopy (Nicolet 5ZDA FTIR) with a tungsten lamp, a quartz beamsplitter, and PbSe detector, was performed on all samples by using a KBr cell. The samples were dried at 55°C for 30 min to remove the residual solvent and moisture.

Raman spectra (RS) were recorded on a Olympus Bx 40 spectrometer. This has a base line of 632.80 nm with 20 mW and another one of 4888 nm with 50 mW.

The UV-spectra of the monomers and polymers were obtained with a Perkin Elmer UV-VIS Scanning Spectrophotometer Lambda 2 of double beam, using solutions of polymers, with concentration ranges from 30−50 mg/l.

The thermal behavior of the polymers was investigated by Differential Scanning Calorimetry (DSC) using a TA instrument, DSQ model. All samples were subjected to the same thermal history, which consisted of a cooling scan from ambient temperature down to −60°C, followed by a heating scan from that temperature up to 100°C.

TABLE 2 Conversion, Molecular Mass Values and Hydroxyl Numbers for Poly(ethyl acrylate) during Polymerization in Presence of 2-Mercaptoethanol

Run	Polymers	Conversion, %	M_n	M_w	$M_w/M_n = PDI$	Hydroxyl number
1	HTPEA-1/1	86	1223	2419	1.98	49
2	HTPEA-1/2	92	1512	2202	1.47	41
3	HTPEA-1/3	94	1211	1567	1.29	48
4	HTPEA-1/4	94	1326	1489	1.12	48
5	HTPEA-1/5	94	2167	4019	1.85	52
6	HTPEA-1/6	95	2234	3023	1.35	46
7	HTPEA-1/7	96	1457	3121	2.14	58
8	HTPEA-1/8	91	1589	2735	1.72	49

M_w, M_n, and M_n/M_w of the polymers by gel permeation chromatography using polystyrene standards.

TABLE 3 Conversion, Molecular Mass Values and Hydroxyl Numbers for Poly(methyl acrylate) during Polymerization in Presence of 2-Mercaptoethanol

Run	Polymers	Conversion, %	M_n	M_w	M_w/M_n	Hydroxyl number
1	HTPMA-1/1	89	1364	2039	1.49	51
2	HTPMA-1/2	91	1491	2202	1.47	36
3	HTPMA-1/3	99	1162	1635	1.41	52
4	HTPMA-1/4	76	1114	1444	1.30	47
5	HTPMA-1/5	75	2093	3392	1.62	50
6	HTPMA-1/6	90	2204	3937	1.77	51
7	HTPMA-1/7	91	1805	2962	1.64	57
8	HTPMA-1/8	82	1758	2697	1.53	48

The heating rate was $10°C/min$ in the all cases. Tg was taken as the midpoint temperature.

RESULTS AND DISCUSSION

Average number molecular weight, Mn, average mass molecular weight, Mw, and polydispersity index PDI of the polymers are listed in
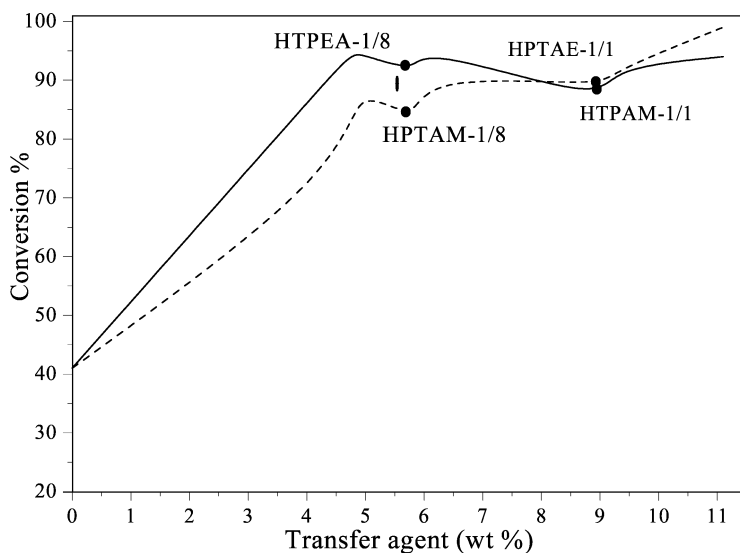
FIGURE 2 Conversion as a function of chain transfer agent in the polymerization of HMTAE and HTPMA.

TABLE 4 Statistical Significance of the Variables for the Different Factors Studied

Variation factors	Conversion	Level of significance	Molecular weight	Level of significance
Main Factors				
Initiator	2.645 NS	0.2453	0.273 NS	0.6586
Monomer	0.106 NS	0.7789	34.422*	0.0278
Transfer agent	3.400 NS	0.2065	137.881**	0.0072
Temperature	28.247*	0.0336	5.815 NS	0.1374
Time	8.576 NS	0.0995	0.407 NS	0.5948

** = Differences are highly significant $P \leq 0.01$, * = Differences are significant $P \leq 0.05$, NS = Differences are non significant.

Tables 2 and 3. From the molecular weight determination, it was observed that the polymers have low molecular weights and medium to high PDI. This may be attributed to reactivity of acrylic groups.

Figure 2 shows the variation of conversion dependence as a function of chain transfer agent in the polymerization of HTPEA and HTPMA (this is common in methacrylate polymerization [17]). Clearly, quite
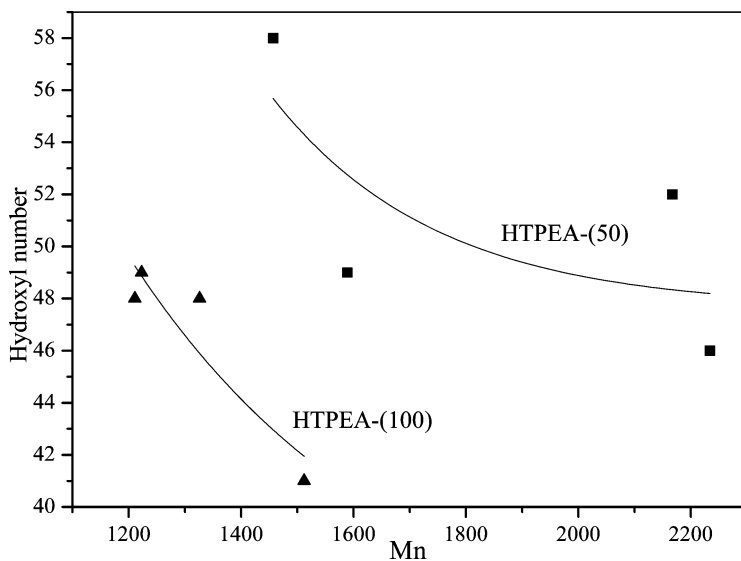
FIGURE 3 Dependence of the hydroxyl number of the HTPEA, on the molecular weight, and 2-MEOH concentration. The 2-MEOH ratios are indicated between brackets.

similar curves were obtained for both the polymerizations of HTPEA and HTPMA. In addition, Figure 1 indicates conversion as a function of transfer agent concentration, indicating that a low initiator concentration plays an important role. This is illustrated for the HTPEA-1/8 (1/1) and HTPMA-1/8 (1/1). The results of Table 4 lead to the conclusion that

1. The factor that most influences the yield is the temperature.
2. The factor that most influences the molecular weight is the transfer agent concentration.
3. The molecular weight shows significant differences as a function of the concentrations of the monomer.

By comparing Tables 1, 2, and 3 one can conclude that the maximum of hydroxyl number is given in the maximum concentrations of the 2-MEOH, attaining the highest value in HTPEA-1/7 and HTPMA-1/7 with 0.24 wt % of chain transfer agent.

The molecular weights of the HTPEA and HTPMA have strong influence on the amount of OH. This is illustrated in Figures 3 and 4. The resulting rate is not remarkably high in the HTPMA-(50), where
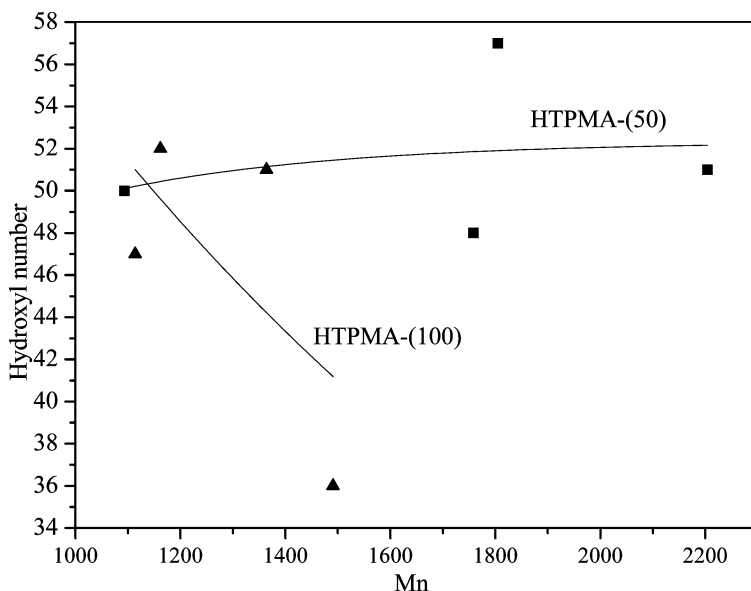
FIGURE 4 Dependence of the hydroxyl number of the HTPMA, on the molecular weight and 2-MEOH concentration. The 2-MEOH ratios are indicated between brackets.
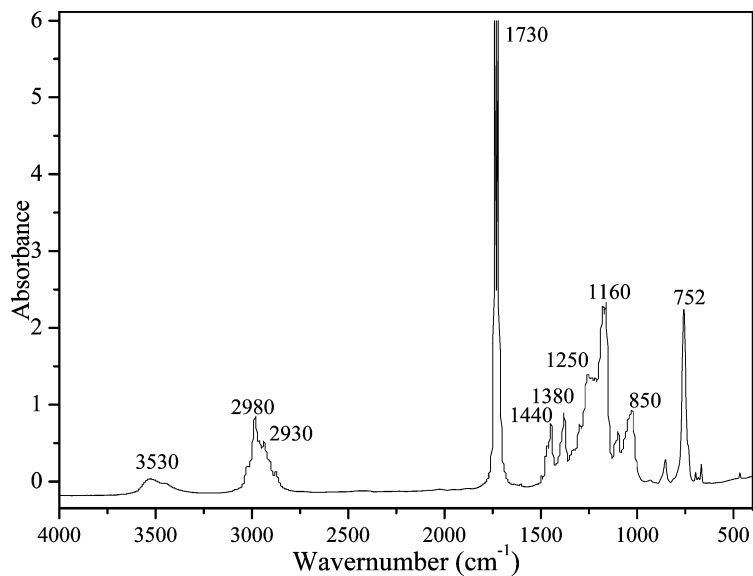
**FIGURE 5** Typical FTIR spectra of hydroxyl-terminated poly(methyl acrylate) oligomers (HTPMA).
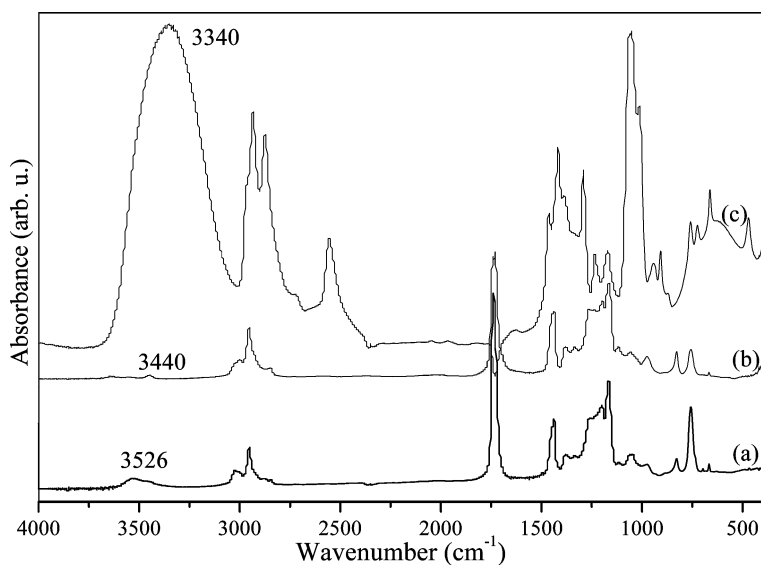
FIGURE 6 IR spectra for: (a) poly(ethyl acrylate) (HTPEA); (b) PEA; and (c) 2-Mercaptoethanol.

TABLE 5 Assignment of Main Absorption Bands
in the IR Spectrum of HTPEA and HTPMA

Absorption peak (cm^{-1})	Assignment
3530	−OH
2980	−CH$_3$
2930	−CH$_2$−
1730	−CO−
1440	−CO−OCH$_3$
1380	−CO−OCH$_3$
1160	−C−CO−O−
1090	−C−O−C−

apparently the inverted slope is explained by the low 2-MEOH concentration. However, the overall tendencies are the same, that is, OH numbers decrease with the molecular weight.

Figure 5 shows the FTIR spectra of HTPMA, where the presence of the bands corresponding to the acrylic polymer can be noticed. The HTPMA spectrum has small differences with respect to the corresponding HTPEA spectrum (Figure 6). The absorption band of hydroxyl groups is broad in the region of 3300−3700 cm^{-1} indicating that the product is polymethyl acrylate single hydroxyl-terminated oligomers, in agreement to the original scheme of Figure 1. The assignment of the main absorption bands of HTPEA and HTPMA appear in Table 5.
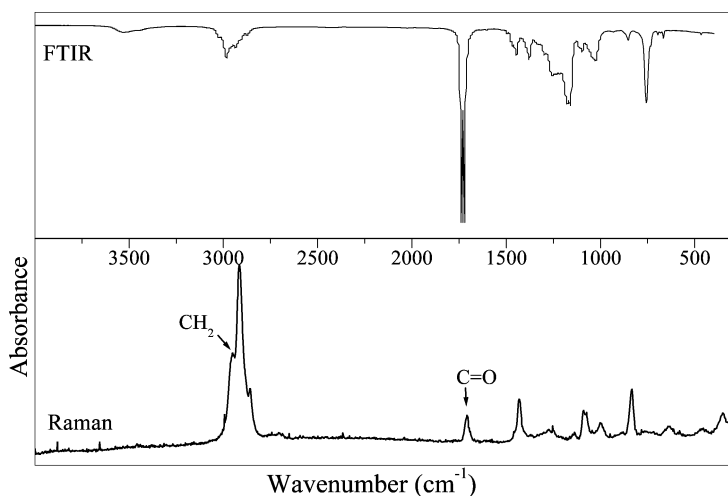
FIGURE 7 Comparison between Raman and infrared spectra of a HTPMA.

A careful comparison of the three spectra in Figure 6 indicates significant differences in the position and magnitude of the IR bands. The spectra obtained from PEA do not reveal the absorption band of hydroxyl groups. In contrast, the 2-MEOH shows the presence of a strong band at $3450-3050$ cm^{-1}. This band (3340 cm^{-1}) is associated to HO stretching vibration, in the $-CH_2CH_2SH$ fragment. In the HTPEA spectrum the strongest intensity band in the region $600-850$ cm^{-1} (765 cm^{-1}) is due both to the wagging vibration of the C=O group [18] and also to the methylene rocking vibration in R-SEt [19]. These results are the strongest evidence of the structure originally intended (Figure 1) and also that all reactants were removed from the sample.

In Figure 7, a comparison between Raman and infrared spectra (both of HTPMA) is presented in order to relate its existent bands and to confirm the chemical structure of the polymers (according to Figure 1).

Although in the RS there is a domain of the C$-$C modes [20], a slight band can be distinguished at $3600-3450$ cm^{-1} that confirms the presence of the hydroxyl groups. This band appears more clearly in Figure 6 whereas the absorption band at $3650-3150$ cm^{-1} due to OH of 2-MEOH [21] compounds had disappeared.

Raman spectroscopy is useful in detecting molecular conformation. Figure 8 shows the effect of tacticity in HTPEA and HTPMA thin films
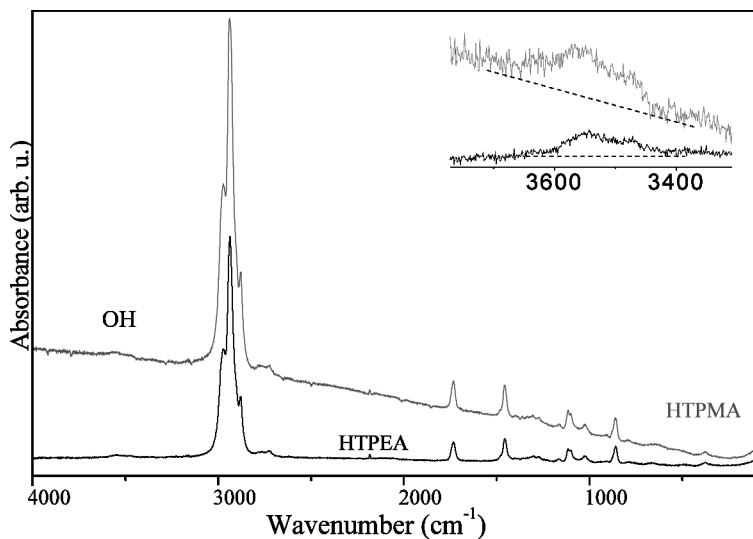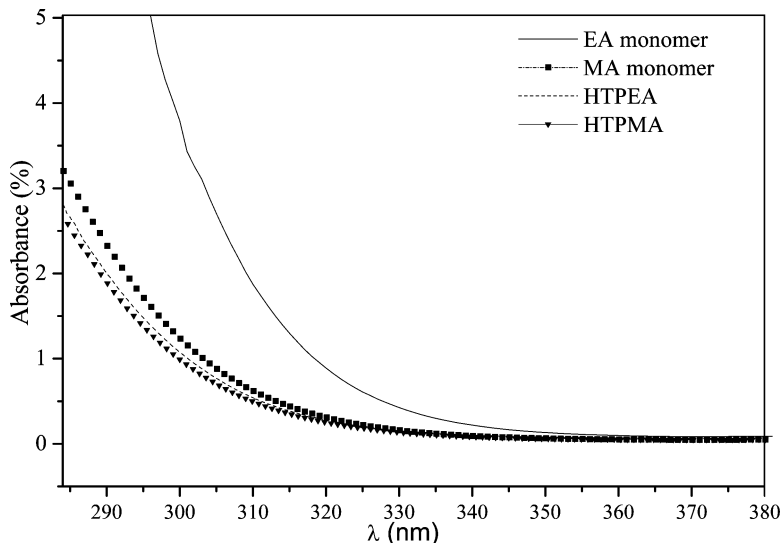

FIGURE 8 Typical Raman spectra of a HTPEA and HTPMA.

FIGURE 9 UV absorption spectra of acrylic monomers (EA and MA) and polymers (HTPEA and HTPMA).

by Raman. The analysis of chain structure reveals an isotactic conformation, which are due the absorption modes at $1800-100$ cm^{-1} [22]. There are other interesting points in Figure 8, namely, the ethylthioethane band due to the $C-C$ rocking vibration (1100 cm^{-1}) and a weak band due to the deformation of the $S-C-C$ group, observed near 375 cm^{-1} [19].

By irradiation with UV light ($270-400$ nm), the rate of decay of the absorbance due to the $C=C$ was measured. The absorption for the bond $C=O$ remained unaffected.

Figure 9 shows the monomers and polymers spectra, in which the maximum absorption correspond to the monomers of EA and MA, as a consequence of their $C=C$ bonds. The effect of polymerization plays an important factor on the rate of absorption. As shown in Figure 9, the differences in intensity may be simply due to differences in the number-concentration of the $C=C$ containing species.

This study illustrated (Figure 9) that the EA monomer has a higher absorption compared to the MA monomer. This result may be attributed to increase in alkyl group. The bathochromic shift, accompanying the alkyl substitution, results from a hyper conjugation, in which the σ-electrons of the alkyl group are mobile enough to interact with the chromophoric group. The extension of conjugation produces further

bathochromic shifts accompanied by an increase in the band intensity [23].

The differential heating of the HTPAE and HTPMA are very similar to each other. The Tg is found approximately between -27 and $-29°C$. These values are lower than those reported in previous references [24] and this allows observation of the influence that the molecular weight (MW) has on the Tg. This influence is expressed by a decrease of the Tg as a consequence of a decrease in the MW. This situation is consistent with that reported in another publication [25], where a decrease in the MW caused a decrease in the Tg. HTPAE and HTPMA show a single thermal transition. This result indicates that in the reaction, secondary products were not generated.

CONCLUSIONS

This study demonstrates how the synthesis of acrylate esters in presence of a 2-mercaptoethanol results in the formation of hydroxyl-terminated polyacrylates oligomers. Therefore, a whole variety of molecular structural differences can be produced, as reveled by FTIR spectroscopy and corroborated by other techniques (RS and UV-VIS).

The statistical design (the 2^2 fractional factorials) were adequate for estimating the optimal molecular mass distribution, hydroxyl number, and conversion (HTPEA 1/7 and HTPMA 1/7) under controlled conditions and with a high grade of certainty. However, the narrow molecular weight distribution (PDI) was broader than expected for an ideal radical polymerization system. This is due to a relatively slow exchange between dormant and active species and termination.

Hydroxyl-terminated polyacrylates oligomers showed similar thermal behaviors regarding their homologous (PEA and PMA) and are apparently unaffected by the hydroxyl pendent group.

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