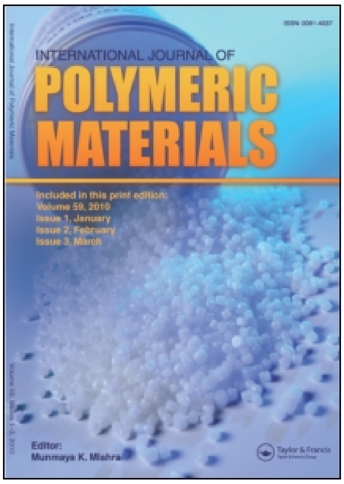

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SYNTHESIS OF COMB-LIKE POLYMERS FROM MACRO-MONOMERS OF ETHYL ACRYLATE-METHYL ACRYLATE AND THEIR PROPERTIES

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SYNTHESIS OF COMB-LIKE POLYMERS FROM MACRO-MONOMERS OF ETHYL ACRYLATE–METHYL ACRYLATE AND THEIR PROPERTIES

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An experimental investigation of comb-like polymers (CP) was conducted in three synthesis steps by using two monomers: ethyl acrylate and methyl acrylate. The synthesis of comb-like homo and copolymers was achieved by using macroinitiators. These compounds imply the formation of hydroxyl terminates polyacrylates (HTP) by a chain transfer reaction. The HTP possessed a broad molecular weight distribution ($Mw/Mn = 1.61$). The CP was freed of its precursors and its molecular weight distribution was rather narrow (1.31–1.44). In addition, the length and number of the "comb" can be controlled. The products were characterized by UV-VIS, FTIR, Gel Permeation Chromatography (GPC), microRaman Spectroscopy (RS), Differential Scanning Calorimetry (DSC), and hydroxyl number titration. The results show that there are situations where it is possible to produce comb-like polymers of interest with high efficiency.

Keywords: oligomers, methyl acrylate, ethyl acrylate, comb-like structures, copolymers, chain transfer agent

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INTRODUCTION

There exists a considerable interest in the production of architecturally designed functionalized polymers. One promising method is that of transfer agent in free-radically initiated polymerization of vinyl monomers. A broad range of chain transfer agents have been explored, including allylic sulfides [1–2] and sulfones [3]. From these chain transfer agents methacrylate macromonomers [4–6] have been obtained.

Comb-like homopolymer and copolymer systems based on association between macromonomers have definite advantages compared to conventional comb polymers systems. They are very easy to synthesize and offer a simple method to vary the number and length of the "combs" by simply varying the oligomer mole fraction x and the length of the oligomers [7]. The possibility to change the morphology of the comb-like polymers gives yet another parameter to tailor the behavior.

Comb-like polymers are generally characterized by having high concentration of chain ends, and having brush-like conformations. Because the backbone chains of these copolymers are sterically shielded, they do not normally aggregate in solution but their long alkyl side-chains crystallize even when their methyl-substituted analogue polymer is amorphous [8–9]. Most of the studies have focused on the nature and behavior of these materials [10–14].

This article considers a homo and copolymer comb-like polymer obtained by free radical polymerization of macromonomers produced by end-functionalized oligomers. The article focuses on a particular system, single hydroxyl-terminated poly(ethyl acrylates) oligomers (HTPEA) and single hydroxyl-terminated poly(methyl acrylates) oligomers (HTPMA). Of these compounds two macromonomers are obtained, ethyl acrylate macromonomer (EA-M) and methyl acrylate macromonomer (MA-M). Finally the EACP, MACP, and EA-MA-CC are obtained, where CP represents comb-like polymers and CC comb-like copolymer.

The reaction scheme that forms the basis of this study is schematically shown in Figure 1. As all steps in a chain polymerization process influence the nature of comb-like polymers produced, the analyses of the characteristics of each step were performed by UV-VIS, FTIR, GPC, microRaman Spectroscopy (RS), DSC, and hydroxyl number titration.

EXPERIMENTAL

Materials

Ethyl acrylate (EA), Methyl acrylate (MA), 2-Mercaptoethanol (2-MEOH), 2′2′ Azobisisobutyronitrile (AIBN),Pyromellitic dianhydride,

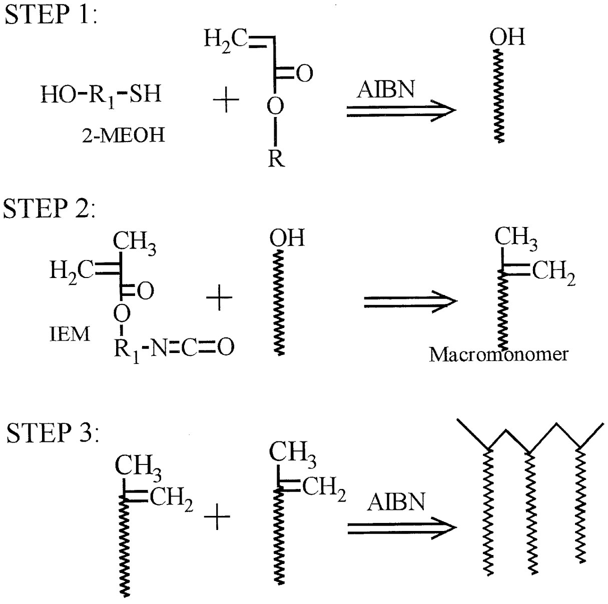

FIGURE 1 Schematical description of comb-like polymer formation by polymerization of macromonomers obtained from HTP. R=CH_3 or $-CH_2CH_3$, R_1=$-CH_2CH_2-$.

Neopentyl glycol (NPG), 1,4 butanediol (1-4 BD) thymol blue, Isocyanatoethyl methacrylate (IEM), and Dibutyltin dilaurate (DBTDL) were purchased from Aldrich. N′N-Dimethyl formamide (DMF) and Imidazole (IMDA) were obtained from Sigma.

Purification of Reagents

Ethyl acrylate and Methyl acrylate was washed twice with 5% NaOH to remove polymerization inhibitor, then twice with $NaHCO_3$, and finally, twice with distilled H_2O. After drying over $MgSO_4$, they were distilled under vacuum and under a nitrogen atmosphere. The initiator, AIBN, was re-crystallized twice from methanol. The chain transfer agents, 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 vacuum under nitrogen atmosphere. Isocyanatoethyl methacrylate and Dibutyltin dilaurate were used as received from Aldrich.

Synthesis Route

As one can see from Figure 1, the comb-like preparation is the result of three synthetic steps.

Synthesis of the Single Hydroxyl-Terminated Polyacrylates (HTPEA and HTPMA)

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 pipetted 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 the purpose of guaranteeing a low molecular weight. The reaction temperature and time were chosen from practical point of view because the acrylates have a very high reactivity [15–16]. Polymerization reactions were run at constant temperature of 55° or 65°C in a preheated oil bath.

By dissolving the reaction products in toluene, precipitating them into a large excess of n-hexane, then redissolving in chloroform, one was able to purify the polymers. After drying at room temperature in a vacuum desiccator for several hours, the products were heated in a vacuum oven at 55 ± 2°C until constant weight. The obtained polymers were clear, transparent, and extremely tacky.

Synthesis of EA and MA Macromonomers (EA-M and MA-M)

To prepare the EA-M and the MA-M in solution, the hydroxyl-terminated polyacrylates (HTP) were added to an apparatus as described earlier. In a typical experiment 30.0 g of HTP were dissolved in 40.0 g of toluene. To this solution were added IEM and DBTDL; the amount of IEM was a 15% excess over the amount of 2-MEOH used in the HTP synthesis, and the concentration of DBTDL was 5.0×10^{-4} wt%.

The reaction flask was a round-bottomed flask with a vertical condenser. It was heated to 60°C in an oil bath, while the reactants were continuously stirred. The reaction was continued for 24 h to completion.

The purification method was carried out as in stage 1. The resulting samples were kept in a desiccator containing fresh $CaCl_2$ until further use.

Synthesis of Comb-Like Polymers (Homo and Copolymers)

Polymerizations and copolymerizations were carried out in a reaction system as the one used in step 1. The AE-CP, AM-CP, and comb-like copolymer of EA-MA (EA-MA-CC) were synthesized by overnight reaction of macromonomers with AIBN, using toluene as solvent.

In order to obtain gel-free polymer the weight ratio of macromonomer/initiator used was 7/3. For the purpose of obtaining an intermediate glass transition temperature (Tg) the weight ratio of EA-M/MA-M used was 48/52.

The purification was carried out as in the step 1. The resulting samples were kept in a desiccator containing fresh $CaCl_2$ until further use.

Characterization Techniques

The molecular weight distribution was determined by Gel Permeation Chromatography (GPC). Polystyrene gel columns 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 HTPEA, HTPMA, and comb-like polymers were analyzed for conversion by gravimetry, measured as percent monomer converted to polymer on a mass basis.

By infrared spectroscope (Nicolet 5ZDA FTIR) with tungsten lamp, a quartz beamsplitter, and PbSe detector, IR measurements were performed using a KBr cell. The slides were dried at 55°C for 30 min to remove the residual solvent and moisture.

Hydroxyl number of polymers HTPEA and HTPMA were determined by the pyromellitic dianhydride method. Pyromellitic dianhydride (PMDA) combine the advantages of both the acetic and phthalic anhydrides, yet its rate of reaction is comparable to that of acetic anhydride. The method was checked with NPG and 1-4 BD [17–18].

Microraman spectra (RS) were recorded by an Olympus Bx 40 spectrometer. This has a line of 632.80 μm with 20 mW of power and the other of 4888 μm with 50 mW of power. The UV-VIS spectra of the monomers and polymers were obtained using a Perkin Elmer UV-VIS scanning Spectrophotometer model Lambda 2 of double beam, and solutions of polymers with concentration ranges 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. The heating rate was 10° C/min in all cases.

RESULTS AND DISCUSSION

Based on a 2^2 statistical factorial designing, eight HTP were obtained in each case. From the molecular weight determination and polydispersity index (PDI), it was observed that both the HTPAE as the HTPAM had a low molecular weight and high PDI (see Table 1). This may be attributed to the reactivity of acrylic groups.

The typical monomer conversions were quite high (near 90%) and no self-acceleration was observed with ethyl acrylate and methyl acrylate. This phenomenon (Tromsdorff) is due to the low viscosity of the polyacrylates. The maximum hydroxyl number is obtained at the maximum concentrations of the 2-MEOH, reaching the highest value with 0.24 wt% of this chain transfer agent. In contrast, a high concentration of the AIBN reduces the number of hydroxyl groups obtained.

On the other hand, the products of the third step generated the values indicated in Table 2. The comb number of polymer was calculated from the following equation:

$$\text{Comb number} = \frac{\text{Polymer (m. w.)} - \text{HTP (m. w.)}}{\text{HTP (molecular weight)}}$$

The conversion percent showed no significant change in dependence of the type of molecular structure (homo and copolymer). The high conversion is due to the molecular weight of the macromonomers, which impeded the evaporation of the reactive mass. Another factor that could have increased the conversion was the high concentration of the solution.

The high concentration of the initiator promoted a high conversion, although it produced a saturated reaction system (therefore a precipitation of the initiator). This allowed the loss of the AIBN and with it the discrepancy with the theoretical expectation in terms of the molecular weight.

TABLE 1 Typical Average Properties of HPTAE and HTPAM, by Considering Eight Samples in Each Case

	HTPAE	HTPAM	Averages
IPD	1.615	1.529	1.572
Mw	2,547	2,664	2,606
Conversion	93	87	90
OH number	49	49	49

TABLE 2 Typical Properties of Comb-Like Homo and Copolymers

	Characteristic comb-like			
HTP o CTP	Molecular weight (Mw)	Comb number	Percent conversion	Macromonomer*
CPAE-1	32,840	10	93	3023
CPAE-2	45,234	15	99	3023
CPAM-1	52,890	24	94	2202
CPAM-2	66,217	30	98	2202
CP-AEAM 1	58,869	24^+	91	3023–2202
CP-AEAM 2	57,363	22^+	97	3023–2202
CP-AEAM 3	62,789	27^+	99	3023–2202

*Precursors of comb-like polymers (CP). Molecular weight of EA = 100.116. Molecular weight of MA = 86.089.

Taking into account the results in Table 2, in some polymers there are reduced number of combs. This result indicates that a star polymer type could have been obtained with reduced molecular weight. This was observed in HTPAE-1 and HTPAE-2.

The progress of polymerization in each reaction step was characterized by FTIR spectra. Figure 2 shows the IR spectra for HTPAE, EA-M, and EA-CP.

The FTIR spectrum of a representative HTPAE indicates the presence of the characteristic bands corresponding to an acrylic polymer.

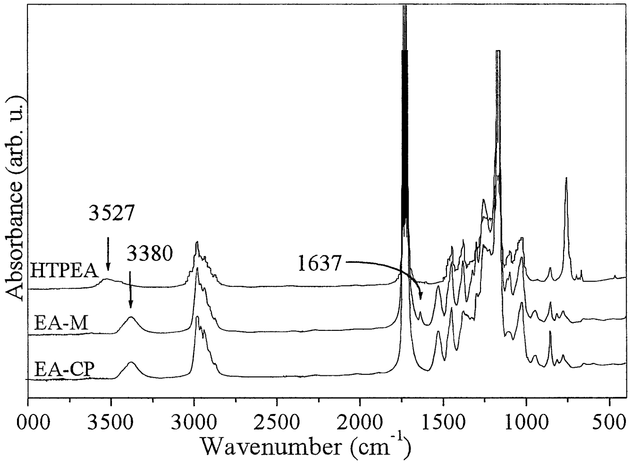

FIGURE 2 FTIR spectra for HTPEA, EA-M, and EA-CP.

It reveals the absorption band of hydroxyl groups that is broad in the region of 3300–3700 cm^{-1} (band at 3527 cm^{-1}), indicating that the product is a single hydroxyl-terminated oligomer.

As a consequence of step 2, the IR spectrum from AE-M indicates the absence of hydroxyl band. This is expected because the hydroxyl group reacts with the isocyanate group. On the contrary, a new adsorption band is observed at a lower wavernumber (3380 cm^{-1}). This band is attributed to the vibration of the NH bond, present in the secondary urethanes (–NH–CO–OR–). This indicates a conversion efficiency of almost 100%. In addition, the peak at 1637 cm^{-1} corresponding to the C=C carbons, shows the presence of double bonds in the EA-M.

The result of step 3 is illustrated in Figure 2. One should note the absorption change of the EA-CP from EA-M. No absorption was observed at 1637 cm^{-1}, indicating that the polymerization of EA-M had happened.

The same chemical changes present in the poly(ethyl acrylate) were also observed in the poly(methyl acrylate). This is illustrated in Figure 3.

A typical spectrum of comb-like copolymer was obtained (Figure 4) in the range of 900–750 cm^{-1}. As a result, it was possible to notice two absorption bands, one at 853 cm^{-1} and the other at 828 cm^{-1}. Furthermore, it was clearly observed that EA-M and MA-M showed a band at 853 cm^{-1} and 828 cm^{-1}, respectively.

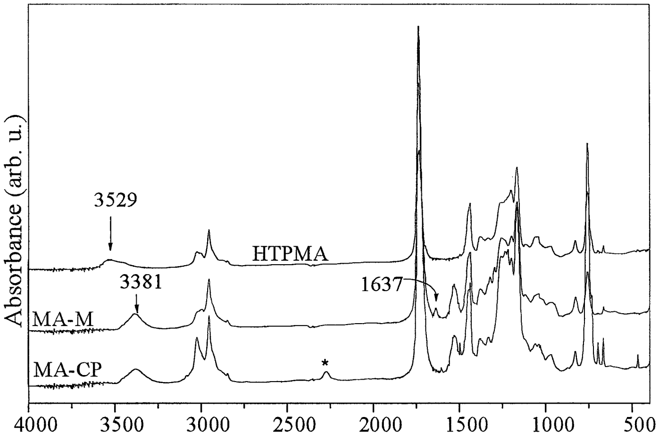

FIGURE 3 FTIR spectra for HTPMA, MA-M, and MA-CP.

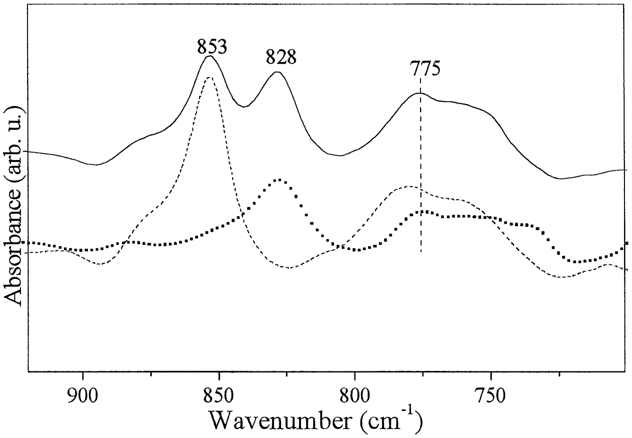

FIGURE 4 FTIR spectra for EACP (——), MACP(■ ■ ■ ■), and EA-MA-CC (—).

The band of the EA-CP at 853 cm^{-1} is inherent to the vibrational mode of the CH_2, regarding the fragment –C(O)–O–CH2–, and the band at 828 cm^{-1} of the MA-CP represents a vibration of the methyl corresponding to the fragment –C(O)–O–CH3 [19]. Evidently, the presence of these two bands in the copolymer could indicate the existence of a hetrogeneous sample. However, due to the unimodality of the curves obtained by GPC, it can be deduced that both macromonomers are chemically connected.

The bands of the comb-like copolymers allow the analysis of the percentage composition of EA-M/MA-M in the copolymer. The absorptions were measured by the base line method. The absorption ratio was 49/51, which was almost identical to the feed ratio (48/52 wt%).

The assignment of the main absorption bands of the different acrylic structures appears in Table 3.

Figures 5 and 6 show the UV spectra of several compounds, where there is an absorption in the range from 280 to 330 nm, indicating the presence of chromophore groups. The chromophore groups that cause this absorption of light in the sample, are mainly those of the type C=O and C=C. In the UV spectra it was noticed that both EA-M and MA-M had an intermediate intensity between their corresponding monomers and HTPs. This situation was less pronounced in the MA-M. These results indicate that C=C group plays an important factor in the absorption process in the macromonomers.

Figure 7 shows the RS spectra for HTPMA and MA-M. The spectra contain bands that can be associated with a typical acrylic polymer

TABLE 3 Assignment of Main Absorption Bands of the Different Acrylic Structures

Absorption peak (cm^{-1})	Assignment
3530	–OH
3370–3270	ν–H
2980	$-CH_3$
2930	$-CH_2-$
1637	$\nu C{=}C$
1730	–CO–
1540–1530	νCHN
1440	$-CO-OCH_3$
1380	$-CO-OCH_3$
1160	–C–CO–O–
1090	–C–O–C–

[20]. A closer look at the spectra of both HTPMA and MA-M in the region of 3700–3400 cm^{-1} reveals that the observed absorption band of HTPMA can be attributed to the hydroxyl groups. In addition, Figure 7 shows that there is one sufficiently isolated MA-M absorption band, at 1642 cm^{-1}, that is suitable for C=C groups deformation analysis. This isolated band is convenient when a quantitative analysis is desired. Nevertheless, in this case Raman spectroscopy provides equivalent information to the FTIR, confirming the structural modification of the oligomer-macromonomer system.

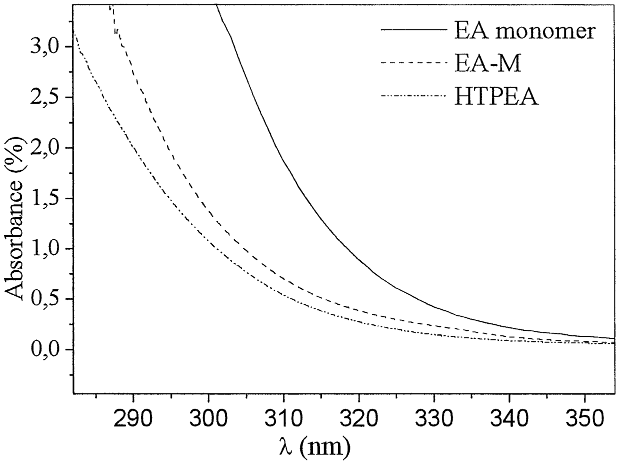

FIGURE 5 UV-VIS spectra of EA monomer, EA-M, and HTPEA.

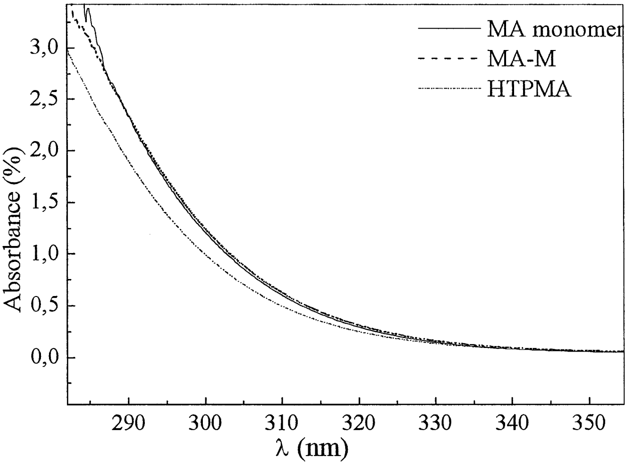

FIGURE 6 UV-VIS spectra of MA monomer, MA-M, and HTPMA.

In all the cases, the Tg of HTPEA is approximately between −27 and −29° C, and the Tg of HTPMA is around 1.44–2.75° C. Although these values are lower than those reported in previous references [21], this allows to observe the influence that the molecular weight (MW) has on the Tg. This influence is expressed by a decrease of the Tg as consequence of a decrease in the MW. This situation is consistent with

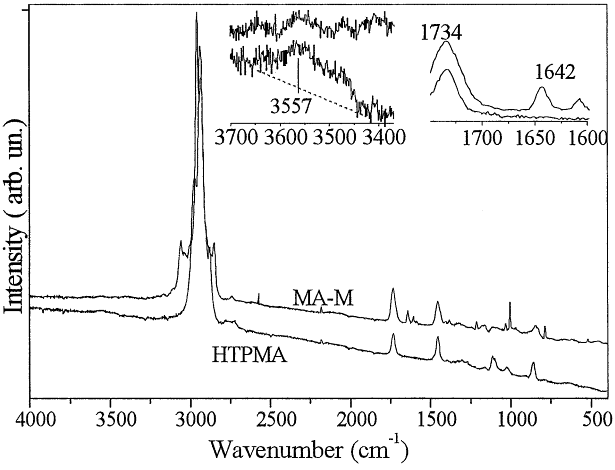

FIGURE 7 Raman spectra of MA-M and HTPMA. Inserts are magnifications where the hydroxyl group and the C=C bonds are present.

that reported in another source [22], where a decrease in the MW causes a decrease in the Tg and in the case of smaller MW the variation of the Tg vs. MW is more important. This effect was quite small in the comb-like polymers because a significant difference did not exist with respect to oligomer precursors.

Based on the number of acrylic units one can estimate the end-to-end distance of each comb based on the conformation energy [23]. For example, the end-to-end distance of the comb contained in a CPAM-1 with 23 MA monomers units is 88.7226 Å (molecular weight 2227.365), with molar volume $1825 \pm 3.0\,\text{cm}^3$.

CONCLUSION

It has been shown that the efficiency of production of end group functionalized polymer (OH) by the addition of chain transfer agent can be rather high. When the transfer agent has the value of 0.24 wt% the efficiency is best. Therefore, chain transfer represents the appropriate factor to manipulate the efficiency. In contrast, fast initiator rate (high concentration of AIBN) results in very low yields of the end group functionalized polymer. Spectroscopy analysis (RS and FTIR) around $3500\,\text{cm}^{-1}$ and around $1640\,\text{cm}^{-1}$, characteristic of OH and C=C groups, confirms the complete HTPEA and HTPMA conversion into acrylic macromonomers. The procedure described here successfully generated a comb-like polymer.

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