Synthesis of acrylic and allylic bifunctional cross-linking monomers derived from PET waste

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Abstract. An acrylic and two novel allylic monomers synthesized from bis (hydroxyethyl) terephthalate, BHET, are reported. This was obtained by glycolysis of post-consumer PET with boiling ethylene glycol. The bifunctional monomer bis(2-(acryloyloxy)ethyl) terephthalate was obtained from acryloyl chloride, while the allylic monomers 2-(((allyloxi)carbonyl)oxy) ethyl (2-hydroxyethyl) terephthalate and bis(2-(((allyloxi)carbonyl)oxy)ethyl) terephthalate, from allyl chloroformate. Cross-linking was studied in bulk polymerization using two different thermal initiators. Monomers were analyzed by means of 1H NMR and the cross-linked polymers by infrared spectroscopy. Gel content higher than 90% was obtained for the acrylic monomer. In the case of the mixture of the allylic monomers, the cross-linked polymer was 80 % using BPO initiator, being this mixture 24 times less reactive than the acrylic monomer.

1. Introduction
Recycling of PET has been widely studied during the last decade due to the huge amounts of PET waste produced globally and because products made from recycled plastics can result in 50–60% energy saving as compared to making the same product from virgin resin [1]. Reusing or recycling of PET packaging can be carried out in different ways. PET containers can sometimes be directly reused as bottles or, on the contrary, its energy content can be recovered by means of incineration. On the other hand, physical recycling involves grinding and melting to obtain different products such as fibers. At this respect, an interesting new approach is the use of PET fibers obtained directly from cutting PET bottles to reinforce cement based materials. A last PET recycling method is their chemical reprocessing, which involves the total depolymerization of waste PET to the monomers, or partial depolymerization to oligomers and other chemical substances [2]. The monomers and oligomers thus obtained can be re-polymerized to produce again PET for packaging applications, or they can be reacted with different monomers to produce starting reactants for a range of different applications. Examples of this chemical reprocessing is the production of unsaturated polyester (UP) resins for polymer concretes and polymer mortars [3], the synthesis of acrylate/methacrylate-terminated oligoesters that could be used as radiation curable oligomers [2], or the formation of alkyd–amino resins for coating applications [4]. In this work we present the synthesis, cross-linking and characterization of an acrylic and two novel allylic monomers, obtained from glycolyzed PET.
through novel synthetic routes, which could be used as cross-linking agents for plastics in order to improve their thermal stability.

2. Experimental

1.1. Synthesis of BAOET
Bis(2-(acryloyloxy)ethyl) terephthalate (BAOET) was synthesized according to the literature [5]. A solution of acryloyl chloride (0.89 g, 9.84 mmol), BHET (1 g, 3.93 mmol) and triethyl amine (0.99 g, 9.84 mmol) in an excess of acetone was placed in a 250 mL one necked round-bottomed flask, with constant stirring and under argon atmosphere during 24 h at room temperature (Figure 1). The reaction mixture was filtered with acetone. The remaining liquid was distilled under reduced pressure and then recrystallized from ethanol-water (2:5), filtered and dried in a vacuum oven at 50 °C to give 1.2 g (3.30 mmol, 83.96 % yield) of yellowish crystals (m.p. 82 -86 °C). 1H NMR (chloroform-d) δ (ppm): 8.15 (s, 4H; aromatic), 4.50 (t, 4H O-CH₂), 4.55 (t, 4H O-CH₂), 6.4 (t, 2H, C=CH), 5.95 (t, 2H, C=CH₂), 6.2 (t, 2H, C=CH₃).

1.2. Synthesis of AOCOEHET and BAOCOET
Allylic monomers were synthesized according to the literature [5]. A solution of allyl chloroformate (1.18 g, 9.84 mmol), BHET (1 g, 3.93 mmol) and pyridine (0.77 g, 9.84 mmol) in an excess of acetone was placed in a 250 mL two necked round-bottomed flask, with constant stirring, under argon atmosphere and using a dean-stark trap during 24 h at room temperature. The reaction mixture was filtered with acetone. The remaining liquid was distilled under reduced pressure, washed with water at 70 °C and dried in a vacuum oven at 50 °C to give 0.55 g (1.4 mmol, 36.11% yield) of a viscous amber liquid, which is a mixture of the monofuntional and bifunctional monomers 2-(((allyloxi)carbonyl)oxy) ethyl (2-hydroxyethyl) terephthalate (AOCOEHET) and bis(2-(((allyloxi) carbonyl)oxy) ethyl)terephthalate (BAOCOET), respectively (Figure 1). The ratio of the mixture is 4:1, AOCOEHET to BAOCOET, according to the 1H NMR spectrum. 1H NMR (chloroform-d) δ (ppm): 8.15 (s, 3.73H; aromatic), 4.48 (t, 2.93H O-CH₂), 4.57 (t, 2.93H O-CH₂), 4.58 (m, 2.93H, O-CH₂), 6.06 (m, 1H, C=CH), 5.28 (m, 1.07H, C=CH₂), 5.42 (m, 1.07H, C=CH₂).

1.3. Bulk polymerization with thermal initiators
BAOET monomer was cross-linked in a quiescent polymerization. Square cells of 3 x 2.5 cm were constructed with two ordinary glass plates. Curable mixtures of BAOET were prepared by dissolving this monomer and two different initiators (benzoyl peroxide, BPO, and azobisisobutyronitrile, AIBN, 2 weight %) in acetone. The liquid mixtures were placed on glass plates, acetone was dried at room temperature, and the resulting solid mixtures were covered with a glass plate and clamped with...
ordinary paperclips. The monomers were polymerized by bulk thermal cross-linking into flat plates of 1-3 mm thickness at a reduced pressure of 42.7 kPa. A Stable Temp Cole-Palmer oven was used for thermal cross-linking at 90 °C.

The allylic monomers were polymerized in sealed Pyrex tubes using benzoyl peroxide (5 weight %) at 90 °C and AIBN (5 weight %) at 70 °C as initiators. Before polymerization, the tubes were degassed by the usual freezing and thawing technique under vacuum and then sealed off. The percentage of insoluble cross-linked polymer formed (gel content) was obtained by extracting the soluble part (sol fraction) from the cured monomer with acetone and filtration. After the extraction, the gel content was dried to a constant weight. Gel content is taken as the weight percent of polymer formed, % gel. Sol and gel fractions were characterized by IR. All the reaction systems were homogeneous before and after the polymerization.

3. Results and discussion

Figure 2a shows the $^1$H NMR spectrum and the assignation of peaks for BAOET. Peaks D, E and F confirm the presence of the acrylic moiety, besides, it can be seen that the monomer is spectroscopically pure through the integration of the signals corresponding to the 4 aromatic protons A and the 8 aliphatic protons C and B. In figure 2b it is observed the spectrum of the mixture of the allylic compounds. Peaks B, C, and D show a lower integration than expected for the bifunctional monomer thus peaks E, F and G show the presence of the allylic groups corresponding to the monofunctional and bifunctional monomers. The ratio AOCOEHET to BAOCOET (4:1) was calculated from the phenylene and allylic protons.

Cross-linked BAOET polymers were characterized by means of FT-IR spectroscopy (Figure 3) using samples with the same weight and also the same polymer:KBr ratio. After 20 min it is still possible to observe the bands at 700 and 3100 cm$^{-1}$ corresponding to the C=C-H and C=C bonds respectively. The comparison of both spectra showed a noticeable intensity decrease, but not absence, of the alkene signals, even though the gel percentage approached 100%.

Figure 4 shows the variation of gel fraction as a function of time for the different monomers using BPO and AIBN. As can be seen, the mixtures of BAOET/BPO and BAOET/AIBN showed similar conversion times, over 90% before 20 minutes of polymerization. On the other hand, the mixture of allylic monomers/BPO reached a conversion nearby 80% after 6 h; when AIBN initiator was used, longer periods were required, obtaining a conversion of 2% after 6 h and, barely, 28% of gel content after 20 h (graph not shown Figure 4).

The noticeable differences between the percentages of gel formed can be due to the fact that the acrylic monomers are much more reactive than the allylic monomers. It is known that these monomers
show an internal inhibition or autoinhibition, which arises from the high resonance stability of the allylic radical formed during the polymerization [6]. It is expected that the cross-linked polymer obtained from the allylic monomer shows better mechanical properties and thermal stability than the crosslinked acrylic polymer due to the presence of the allylcarbonate moiety [5]. On the other hand, it seems that BPO is a better initiator for the allylic polymerization probably due to the fact that the half-life of AIBN is much lower than the half-life of BPO at the temperatures used during the polymerization [6]. Finally, it is possible that the presence of the monofunctional allylic monomer could also interfere in the common cross-linking behavior of the bifunctional monomer. Since the yield is still low for the allylic monomers, 13% for the bifunctional and 51% for the monofunctional, further work is being done in order to obtain a higher yield for the bifunctional monomer. The yield for the acrylic monomer was 83.6%.

Figure 3. FT-IR spectra of BAOET polymer after 5 min (dot line) and 20 min (solid line). Arrows indicate the characteristic absorption bands of alkene groups bonds.

Figure 4. Cross-linking average of the mixtures of monomers with thermal initiators as a function of time: BAOET/BPO, BAOET/AIBN and BAOCOET/AOCOEHET/BPO

4. Conclusions
BHET obtained from PET depolymerization can be used to obtain bifunctional acrylic and allylic monomers, which could be used as cross-linking agents. In the case of the acrylic monomer, cross-linking rate and gel content is similar using both AIBN and BPO initiators, but for the allylic monomer cross-linking rate and gel content is faster using BPO than using AIBN. Cross-linking degree is higher for the acrylic monomer than for the mixture of allylic monomer, due to their different reactivities and to the presence of the monofunctional allylic monomer.

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6. References
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