Preparation of Tailor-Made Multifunctional Propenyl Ethers by Radical Copolymerization of 2-(1-Propenyl)oxyethyl Methacrylate

S. Vansteenkiste,[†] G. Matthijs,[†] E. Schacht,*,[†] F. C. De Schrijver,[‡] M. Van Damme,[§] and J. Vermeersch[§]

Polymer Materials Research Group, Department of Organic Chemistry, Faculty of Science, University of Gent, Krijgslaan 281 S4bis, B-9000 Gent, Belgium, Laboratory for Molecular Dynamics & Spectroscopy, Department of Chemistry, Faculty of Science, Catholic University of Leuven, Celestijnenlaan 200F, B-3001 Heverlee, Belgium, and Agfa-Gevaert N.V., Septestraat 27, B-2640 Mortsel, Belgium

Received March 24, 1998; Revised Manuscript Received October 27, 1998

ABSTRACT: A new approach for preparation of multifunctional polymers with pendant vinyl ethers was investigated. In particular, 2-(1-propenyl)oxyethyl methacrylate, a new ambifunctional monomer combining easy radical polymerization and a fast cationically cross-linkable group, was evaluated. Hence, the physical characteristics of copolymers were controlled by the selection of comonomers. Cross-linking kinetics as a function of temperature and concentration of the acid-generating species were monitored quantitatively by FT-IR spectroscopy. Through the use of DSC measurements, the onset for cationic polymerization was determined. It was demonstrated that both 9-fluorenylideneimino-*p*-toluenesulfonate and diphenyliodonium triflate could be used as efficient thermally initiating cross-linking agents.

Introduction

During the past decade, the thermally initiated and photoinitiated cross-linking polymerization has become a useful technique for the rapid curing of coatings, adhesives, and inks in many research areas such as lithography and printing applications. Many of the existing systems include the radical UV-photoinitiated cross-linking of polyfunctional (meth)acrylates. Despite their advantageous reaction kinetics, several drawbacks such as toxicity and oxygen inhibition still remain.

On the other hand, a lot of experimental data concerning photochemically and thermally induced polymerization of cationic polymerizable monomers has become available recently. In the literature, the attractiveness of multifunctional vinyl,[1,2] 1-propenyl,[3−5] and 1-butenyl ethers[6] as cationically cross-linkable additives is demonstrated extensively. These reactive functions showed, in contrast with epoxy groups, polymerization rates which are similar to those of methacrylic systems.[7]

However, most of the reported vinyl or propenyl ethers are low molecular weight products. They are commonly used as diluents to acrylates in curing applications. Therefore, it is considered that polyfunctional vinyl or propenyl ether compounds of high molecular weight will offer advantages such as compatibility and low odor. In the literature, reactive polymers containing pendant vinyl groups with a polyester[8] or polyurethane[9] backbone are described. In this paper, we focused our research work on the synthesis of methacrylates with pendant propenyl ethers. In particular, an ambifunctional monomer combining easy radical polymerization with a fast cationically cross-linkable moiety was evaluated. This approach offers the possibility for the radical copolymerization of tailor-made polymers with propenyl ether side groups. Hence, multifunctional polymers with a wide variety of physicochemical properties such as solubility, glass transition temperature, propenyl ether content, or compatibility with acid-generating agents are devisable by selection of comonomers.

The ambifunctional monomers vinyloxyethyl acrylate (VOEA)[10] and the methacrylate analogue (VOEMA)[11] are both described in the field of the living cationic polymerization of vinyl ethers with pendent (meth)acrylates. The synthesis of multifunctional vinyl monomers containing more than two vinyl groups is also reported.[12] The authors demonstrated the photopolymerization of the monomers, induced by either radical or cationic initiators which form interpenetrating networks. To our knowledge, such monomers were never applied to the preparation of tailor-made multifunctional vinyl ethers. Therefore, a synthetic route was worked out for the preparation of 2-(1-propenyl)oxyethyl methacrylate (POEMA). Because both the radical and cationic polymerization behavior of VOEMA and POEMA is quite similar,[13] this paper is limited to the investigation of POEMA.

Experimental Section

Measurement. The average molecular weights M_n and M_w of the copolymers were determined by gel permeation chromatography (GPC) on a PL-gel mixed D-5μ 7.8 × 600 mm column calibrated by polystyrene standards and chloroform as an eluent without correction using a MELZ LCD-212 refractive index detector. ^{1}H and ^{13}C NMR measurements were carried out on a Bruker AM 360 MHz instrument with tetramethylsilane as an internal standard. Infrared measurements were made on a Perkin-Elmer 1600 series FT-IR spectrometer. Thermographic analysis (TGA) was performed on a T.A. Instruments Hi-Res TGA-2950 apparatus under nitrogen flow using a temperature gradient of 10 °C/min. Differential scanning calorimetric (DSC) data were obtained using a T.A. Instruments modulated DSC-2920 apparatus. Mass spectrometry was carried out on a Hewlett-Packard 5988A system at 70 keV.

Materials. Dimethyl sulfoxide (Acros Chimica, Geel, Belgium) was dried over calcium hydride and distilled in vacuo

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[†] University of Gent.
[‡] Catholic University of Leuven.
[§] Agfa-Gevaert N.V.

10.1021/ma980458+ CCC: $18.00

prior to use. Toluene (Acros Chimica) was refluxed over sodium for 12 h and then distilled. Styrene and butyl methacrylate (Acros Chimica) were purified by vacuum distillation before use. Methacrylic anhydride and octadecyl methacrylate (ODMA) were purchased from Aldrich (Bornem, Belgium) and were purified by vacuum distillation before use. All other chemicals ware purchased from Acros Chimica and were used as commercial grade. Diphenyliodonium triflate was prepared as described in the literature.[14,15] 9-Fluorenylideneimino-*p*-toluenesulfonate was synthesized according to the method of Schwan and Burch[16] and Shirai et al.[17]

Synthesis of 2-Hydroxyethyl Allyl Ether (1). To a solution of sodium hydroxide (120 g, 3 mol) in 840 mL of ethylene glycol was added dropwise with stirring 260 mL (3 mol) of allyl bromide. The reaction mixture was left at 100 °C for 24 h. The mixture was cooled to room temperature and poured into an excess of water. By repeated extraction with pentane, all ethylene glycol diallyl ether was removed from the mixture. Subsequently, 2-hydroxyethyl allyl ether was extracted with diethyl ether. The ether layer was dried over anhydrous magnesium sulfate and concentrated under reduced pressure. Finally, 2-hydroxyethyl allyl ether was purified by vacuum distillation (bp: 58−60 °C at 20 mmHg). Yield: 187 g (61%). IR (neat, cm^{-1}): 3412 (ν_{OH}), 3080 ($\nu_{=C-H}$), 2923, 2863 (ν_{CH_2}), 1645 ($\nu_{C=C}$), 1112 (ν_{C-O}), 1066 (ν_{C-O}). ^1H NMR (360 MHz, acetone-d_6, TMS): δ (ppm) 5.85 (m, 1H, $-CH=CH_2$), 5.21 and 5.06 (m, 2H, $-CH=CH_2$), 3.94 (m, 2H, $OCH_2CH=CH_2$), 3.63 (m, 3H, *H*O− and $HOCH_2-$), 3.44 (m, 2H, $-CH_2CH_2O-$). ^{13}C NMR (90 MHz, acetone-d_6, TMS): δ (ppm) 135.75 (allyl, $-CH=$), 115.61 (allyl, $CH_2=$), 72.00 and 71.73 ($-CH_2OCH_2-$), 61.36 ($-CH_2OH$). MS (70 keV, *m*/*e*): 71 (M^+, $-CH_2OH$), 57 (M^+, $-CH_2CH_2OH$), 41 ($M+ - HOCH_2CH_2O$).

Synthesis of 2-Hydroxyethyl 1-Propenyl Ether (2). A well stirred solution of **1** (51.06 g, 0.5 mol) and potassium *tert*-butoxide (118 g, 1 mol) in 500 mL of dimethyl sulfoxide (DMSO) was heated to 100−110 °C for 1 h. The mixture was cooled to room temperature and poured into 2 L of water. By repeated extraction with diethyl ether/pentane (1/1, v/v), the *cis*-1-propenyl ether can be obtained. Subsequently, the organic layer was dried over anhydrous magnesium sulfate, and the solvent was removed under reduced pressure. Finally, the 2-hydroxyethyl 1-propenyl ether was purified by vacuum distillation (bp: 60 °C, 15 mmHg). Yield: 30 g (60%). IR (neat, cm^{-1}): 3380 (ν_{OH}), 3043 ($\nu_{=C-H}$), 2926, 2875 (ν_{CH_2,CH_3}), 1668 ($\nu_{C=C}$), 1134 (ν_{C-O}). ^1H NMR (360 MHz, acetone-d_6, TMS): δ (ppm) 5.99 (q, 1H, *cis*-propenyl ether, $-OCH=CH-$), 4.25 (m, 1H, $-OCH=CH-$), 3.75 (m, 3H, *H*O− and $-CH_2O-$), 3.64 (m, 2H, $HOCH_2-$), 1.46 (d, 3H, $-CH_3$). ^{13}C NMR (90 MHz, acetone-d_6, TMS): δ (ppm) 147.02 ($-OCH=$), 100.50 ($=CH-$), 74.25 ($-CH_2O-$), 61.91 ($HOCH_2-$), 9.31 ($-CH_3$). MS (70 keV, *m*/*e*): 102 (M^+), 71 (M^+, $-CH_2OH$), 57 (M^+, $-CH_2CH_2OH$), 45 (M^+, $-OCH=CHCH_3$).

Synthesis of 2-(1-Propenyl)oxyethyl Methacrylate (POEMA) (3). To a solution of **2** (15 g, 0.147 mol) in 200 mL of dichloromethane were added with stirring methacrylic anhydride (22.6 g, 0.147 mol) and triethylamine (22.7 mL, 0.15 mol). The reaction was left overnight. The reaction mixture was extracted twice with a saturated $NaHCO_3$ solution and once with water. After the organic layer was dried over anhydrous magnesium sulfate, 3 mL of 2-aminoethanol was added. Subsequently, the dichloromethylene phase was extracted twice with water and dried over anhydrous magnesium sulfate. Finally, the mixture was concentrated under reduced pressure, and the 2-(1-propenyl)oxyethyl methacrylate was purified by vacuum distillation (bp: 60 °C, 0.5 mmHg). Yield: 20.5 g (82%). IR (neat, cm^{-1}): 3044 ($\nu_{=C-H}$), 2955, 2927, 2873 (ν_{CH_2,CH_3}), 1721 ($\nu_{C=O}$), 1670 ($\nu_{C=C}$), 1168 (ν_{C-O}). ^1H NMR (360 MHz, acetone-d_6, TMS): δ (ppm) 6.13 and 5.56 (d, 2H, $CH_2=$), 5.95 (d, 1H, *cis*-propenyl ether, $-OCH=CH-$), 4.42 (m, 1H, $-OCH=CH-$), 4.30 (t, 2H, $-COOCH_2-$), 3.95 (t, 2H, $-CH_2OCH-$), 1.94 (s, 3H, $-CH_3$), 1.56 (d, 3H, $=CH-CH_3$). ^{13}C NMR (90 MHz, acetone-d_6, TMS): δ (ppm) 167.1 (C=O), 145.2 ($-OCH=$, propenyl ether), 136.0 ($CH_2=C-$, vinyl), 125.7 ($CH_2=C-$, vinyl), 102.1 ($=CH-$, propenyl ether), 69.4 ($-COOCH_2$), 63.5 ($CH_2OCH=$), 18.1 ($-C-CH_3$), 9.0 ($-CH-CH_3$). MS (70 keV, *m*/*e*): 170 (M^+), 113 (M^+, $-OCH=CHCH_3$), 69 (M^+, $-OCH_2CH_2OCH=CHCH_3$), 41 (M^+, $-COOCH_2CH_2OCH=CHCH_3$).

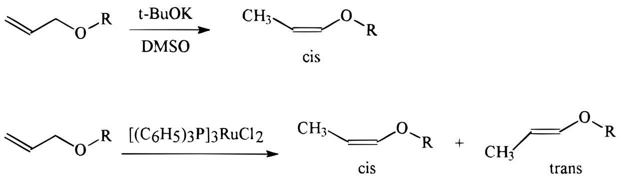


Figure 1. General pathway for the preparation of 1-propenyl ethers by isomerization of the corresponding allyl compound.

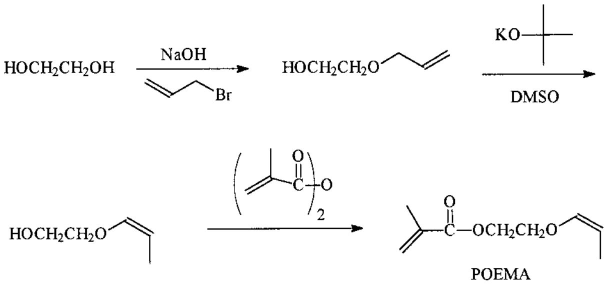


Figure 2. Synthetic route to 2-(1-propenyl)oxyethyl methacrylate (POEMA).

Synthesis of 2-(1-Propenyl)oxyethyl Methacrylate (POEMA) Copolymers (4a). A solution of 2.45 g of POEMA (14.4 mmol), 1.70 g of octadecyl methacrylate (ODMA) (5.0 mmol), 3.06 g of methyl methacrylate (MMA), and 38.8 mg of 2,2′-azobisisobutyronitrile (0.24 mmol) in 20 mL of toluene was deoxygenated by flushing with N_2. The mixture was heated overnight to 65 °C. The resulting copolymer was isolated by precipitation in an excess of MeOH and theb dried under vacuum. Yield, >95%.

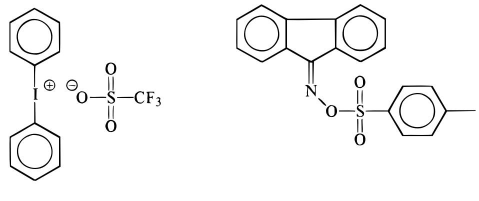
The composition of the copolymer was determined by the ratio of diagnostic resonances in the corresponding ^1H NMR spectrum. Generally, the polymeric composition reflected the initial ratio of comonomers as was anticipated for high conversion yields. IR (neat, cm^{-1}): 3044 ($\nu_{=C-H}$), 2955, 2927, 2873 (ν_{CH_2,CH_3}), 1730 ($\nu_{C=O}$), 1670 ($\nu_{C=C}$), 1168 (ν_{C-O}). ^1H NMR (360 MHz, $CDCl_3$, TMS): δ (ppm) 5.95 (1H, *cis*-propenyl ether, $-OCH=CH-$), 4.45 (1H, $-OCH=CH-$), 4.10 (2H, $-COOCH_2-$) for POEMA; 3.95 (2H, $-COOCH_2-$) of ODMA and (2H, $-CH_2OCH-$) of POEMA; 3.60 (3H, $-CH_3$) of MMA. GPC: M_w = 73 000 and M_n = 45 600 (M_w/M_n = 1.60).

Results and Discussion

Synthesis of 2-(1-Propenyl)oxyethyl Methacrylate (POEMA) (3). Over the past decade, Crivello and co-workers have described the synthesis of a wide variety of multifunctional 1-propenyl ethers. The latter compounds are readily prepared from the corresponding allyl ethers by straightforward isomerization of the allyl double bond as shown in Figure 1.

Through the use of base catalysis, isomerization results in the exclusive formation of the cis isomer, but the corresponding tris(triphenylphosphine)ruthenium(II) dichloride catalyzed reaction gives a mixture of cis and trans isomers. Recently, the preparation of **3** starting from allyl methacrylate was attempted.[18] However, during the ruthenium catalyzed isomerization, which proceeded at 190 °C for 20 min, an uncontrollable polymerization of the methacrylate monomer could not be avoided. Therefore, an alternative synthetic route was devised in which the isomerization reaction at elevated temperature is carried out before the introduction of the methacrylate ester (Figure 2).

Selective monoallylation of ethylene glycol could be obtained in good yields (60%) using a 5-fold excess of ethylene glycol. Undesired diallylethylene glycol was



(A) (B)

Figure 3. Chemical structure of the selected thermal acids: (A) diphenyliodonium triflate (DIT) and (B) 9-fluorenylidene-imino-*p*-toluenesulfonate (FITS).

removed selectively by extraction with pentane. The potassium *tert*-butoxide catalyzed isomerization was conducted in DMSO at 120 °C for 1 h yielding exclusively *cis*-propenyl ether. Longer reaction times resulted in a great reduction of the yield of the product. As reported in the literature,[19−21] an extra molar equivalent of *tert*-butoxide was used for each hydroxyl function present in the substrate in order to obtain a satisfactory conversion rate. Subsequently, the esterification of **2** was carried out using methacrylic anhydride as an acylating reagent. The use of methacryloyl chloride resulted in an undesired addition of hydrochloric acid to the 1-propenyl ether double bond.

Radical Copolymerization of POEMA (4). A number of POEMA copolymers were prepared with a wide variety of comonomers such as (meth)acrylates, acrylamides, or styrene. Nevertheless, attempts to homopolymerize POEMA were unsuccessful because of cross-linking during polymerization. Furthermore, it was observed that both the molecular weight and the molecular-weight distribution of the copolymers increased with increasing POEMA content. Transfer of the allylic hydrogen, radical polymerization of the 1-propenyl ether double bond, or both together probably resulted in the undesired product.

Study of the Thermally Initiated Cross-Linking of 4. In this paper, the authors focus on the thermally initiated curing of MMA/ODMA/POEMA (45/25/30; wt %) copolymer. The 1-propenyl ether content of 30 wt % allowed us to investigate the cationic thermal curing by IR and DSC measurements. Frequently used thermally latent initiators for cationic processes include diaryliodonium, sulfonium, and or ammonium salts with nonnucleophilic counterions.[22,23] From these numerous examples, diphenyliodonium triflate (DIT) (Figure 3) was selected on the basis of its excellent solubility in organic solvents and its appropriate decomposition temperature. However, because of the strongly ionic nature of "onium"-type acid generators, incompatibility with highly hydrophobic matrixes often occurs. Recently, extensive analytical data published by Atalla[24,25] demonstrated the formation of sulfonic acid by pyrolysis of ketoxime arenesulfonates. Therefore, in this study we also highlight the application of 9-fluorenylideneimino-*p*-toluenesulfonate (FITS) (Figure 3) as an example of a novel class of a nonionic, thermally initiating species for propenyl ethers. The effectiveness of both types of thermal initiators as a function of temperature and concentration was investigated by DSC measurements. The kinetics of thermally induced cross-linking was studied in situ by FT-IR spectroscopy.

The thermally induced curing of **4** was carried out by transmission FT-IR using 1% w/w FITS. Therefore, an 8% w/w solution in methyl ethyl ketone was prepared and coated onto the KBr substrate. The KBr was conditioned at 130 °C, and the sample was monitored at regular time intervals (2.5 min). The conversion of the propenyl ether groups was estimated from the decrease of the absorbance at 1670 cm^{-1}.

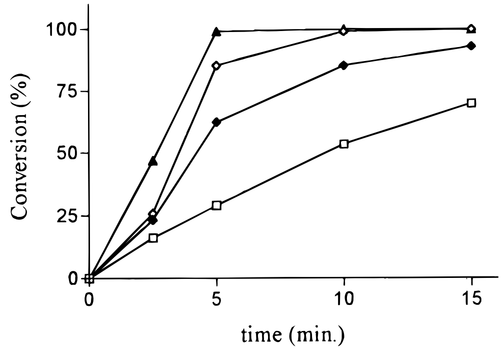


Figure 4. Effect of the concentration of FITS on the polymerization rate of **4** as studied by FT-IR: □, +0.5%; ◆, +1.0%; ◇, +2.0%; ▲, +5% (w/wt % FITS).

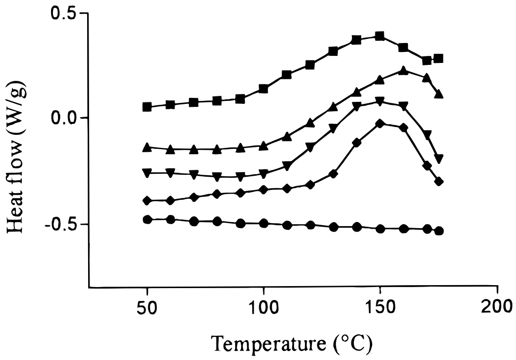


Figure 5. Effect of the concentration of FITS on the polymerization rate of **4** as studied by DSC: ●, blank; ◆, +0.5%; ▼, +1.0%; ▲, +2.0%; ■, +5.0% (w/wt % FITS).

The effect of the FITS concentration on the conversion of **4** is exhibited in Figure 4.

The reaction proceeded smoothly in the presence of 0.5% w/w FITS. A conversion of 50% after 10 min was obtained. The reaction rate increased with an increase of the FITS concentration. In the presence of 1% w/w FITS, an 80% conversion of the propenyl moieties was observed after 10 min of heating. A complete disappearance of the propenyl groups after 10 min was obtained by using a 2% w/w FITS concentration. The extent of the polymerization rate further increased with larger thermal acid contents: adding 5% w/w of FITS resulted in a 100% yield after only 4 min.

A supplementary DSC study was conducted to determine the onset polymerization temperature of **4**. The results of this thermal analysis are shown in Figures 5 and 6.

It is clear that the presence of a thermal initiator causes an exothermic process at 120 °C, which is attributed to the heat of polymerization of the pendant 1-propenyl ethers. In contrast with DIT, the exothermic peak in the presence of FITS showed a heading from 100 °C, which becomes more pronounced with the increasing content of the latent initiator. The maximal heat flow remains almost constant around 150 °C. This observation is explained by the inferior thermal stability of FITS compared with that of the onium salt. The contrast of the thermal lability of the nonionic acid generators with that of onium salts is well-documented in the literature.[26] A similar effect is seen in the case of DIT at low concentrations (0.5 and 1.0 wt %), resulting

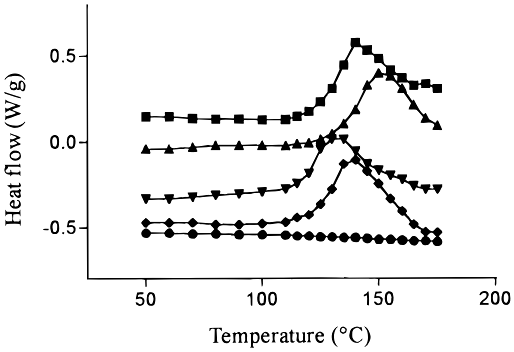


Figure 6. Effect of the concentration of DIT on the polymerization rate of **4** as studied by DSC: ●, blank; ◆, +0.5%; ▼, +1.0%; ▲, +2.0%; ■, +5.0% (w/wt % DIT).

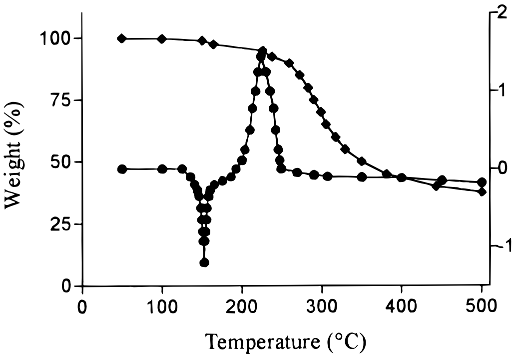


Figure 7. TGA-DSC analysis of FITS: ◆, TGA curve; ●, DSC curve.

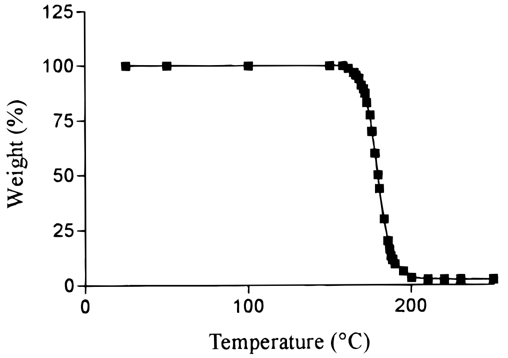


Figure 8. TGA analysis of DIT.

in both a lower onset temperature (110 °C) and a lower maximal heat flow. At higher DIT concentrations, an upward shift is observed. This can be explained by the incompatibility of the iodonium salt in the polymer matrix, resulting in a partial phase separation.

The onset temperatures of polymerization in the presence of FITS and DIT, shown in Figures 5 and 6, were 50 °C lower than the onset decomposition temperatures measured by TGA−differential scanning calorimetry (DSC) represented in Figures 7 and 8. The DSC curve of FITS shows two major transitions: the first at 152 °C is endothermic and corresponds to the melting point whereas the second transition appears almost immediately after the melting step. The latter is strongly exothermic and is attributed to the decomposition of the material. This decomposition is also confirmed by the TGA curve, which shows the start of a substantial weight loss occurring on heating FITS above its melting point.

A decrease of the decomposition temperature of thermal initiators was already reported by Barclay and co-workers[27] for the analogous sulfonate ester, which was applied as an acid generator in phenol matrixes. However, no correlation between the onset of decomposition as determined by DSC and the weight loss as observed by TGA was reported. The often large discrepancies were explained by the nonvolatile nature of the thermal degradation products. Nevertheless, through the use of DSC, a reduced thermal stability of sulfonate esters in a phenolic environment was observed compared to the neat samples. Moreover, this study supported a decomposition mechanism, which involves a nucleophilic attack by the phenolic moieties at the sulfonate ester linkage, resulting in the liberation of sulfonic acid. Hence, this rationale cannot be correlated to the inert matrix of copolymer **4**. Therefore, a possible explanation is that the thermal stability of the acid generator if dissolved in a polymer matrix is lower than if it is in the neat crystalline state. This hypothesis is supported by recent data of Fréchet and co-workers.[28] Moreover, by accepting this rationale, the reduced decomposition temperature of DIT at low concentrations can also be explained. In this case, the onset of initiation is 120 °C, and the melting point[29] followed immediately by fragmentation is at 180 °C, as is shown in Figure 8.

Conclusions

A new amphiphilic monomer 2-(1-propenyl)oxyethyl methacrylate was prepared successfully by isomerization of 2-hydroxyethyl allyl ether using base catalysis and subsequent esterification with methacrylic anhydride. Radical copolymerization of 2-(1-propenyl)oxyethyl methacrylate offers the possibility to prepare a wide variety of multifunctional 1-propenyl ethers by selecting the accompanying monomers. It was demonstrated that the reactive copolymers obtained were cross-linked quickly in the presence of latent cationic thermal initiators such as diphenyliodonium triflate and 9-fluorenylideneimino-*p*-toluenesulfonate. It was also concluded that the decomposition temperature of the thermal initiators was considerably lower in a polymer matrix than in the neat crystalline state.

Acknowledgment. The authors thank the Flemish Institute for the Promotion of Scientific-Technological Research in Industry (IWT), the Fund for Scientific Research-Flandern (FWO), and the Belgian Ministry of Scientific Programming, IUAP/PAI-IV/11, for their financial support.

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