Polymer Bulletin 32, 403–410 (1994)

Polymer Bulletin

Preparation and cure behavior of dimethacrylates containing oligo(tetrafluoroethene) segments

Norbert Steinhauser and Rolf Mülhaupt*

Freiburger Materialforschungszentrum und Institut für Makromolekulare Chemie,
Stefan-Meier-Strasse 31, D-79104 Freiburg, Germany

Summary

Two novel families of dimethacrylate-based thermoset resins containing oligo(tetrafluoroethene) segments with n= 1, 2, 3 tetrafluoroethene units were prepared from dimethyl tetrafluorosuccinate, dimethyl octafluoroadipate and dimethyl dodecafluorosuberate. Methacrylate functionalities were determined using ^{1}H-NMR spectroscopy. Photocrosslinking by UV irradiation in the presence of photoinitiators affords amorphous networks. The influence of the oligo(tetrafluoroethene) segment length on glass transition temperatures, swelling, volume shrinkage and thermal degradation was investigated.

Introduction

Linear and crosslinked polymers containing perfluoroalkylene segments are well known to exhibit unusual property synergisms, e.g., high chemical, thermal and environmental stabilities combined with low water up-take, high oxygen permeabilities, abrasion resistance, and low flammability. Since the discovery of poly(tetrafluoroethene) by Plunkett at Du Pont, the major research and development emphasis has been placed upon chain growth polymerization of fluorine-containing monoolefins (1). Much less is known about the properties of polymeric networks derived from difunctional perfluoroalkylenes because of the rather limited availability of the corresponding fluorine-containing difunctional oligo(tetrafluoroethene) intermediates. Today, tetrafluoroethene oligomerization in the presence of diiodo-terminated perfluoroalkanes as telogens represents the preferred route to difunctional intermediates (2,3). Recently, Millauer (4) developed an efficient electrochemical process in which fluorosulfonic acid is oxidized electrochemically to form the peroxodisulfuryldifluoride as initiator for tetrafluoroethene oligomerization. As a result of the predominant radical recombination, difunctional intermediates such as di(fluorosulfato)-, diester-, or diacidhalide-terminated oligo(tetrafluoroethenes) are obtained in high yields and high purities. The objective of our research was to exploit the potential of Millauer's intermediates and to prepare a family of dimethacrylate-terminated oligo(tetrafluoroethene)s with n=1, 2, 3 tetrafluoroethene structural units. Moreover, the cure behavior of this new type of thermoset resins and the influence of the oligo(tetrafluoroethene) segment length on monomer and polymer properties were investigated.

---

*Corresponding author

Experimental

Materials: Dimethyl tetrafluorosuccinate (n = 1, b.p. 58-59 °C at 10^3 Pa), dimethyl octafluoroadipate (n = 2, b.p. 80-81 °C at 10^3 Pa), and dimethyl dodecafluorosuberate (n = 3, b.p. 100-101 °C at 10^3 Pa) were obtained from Hoechst AG and purified by distillation. All compounds were prepared and stored under a dry argon atmosphere.

Preparation of dimethacrylates **1**: N,N'-bis(5-hydroxypentyl)-2,2,3,3-tetrafluorosuccinic diamide was prepared by adding within few minutes 8.98 g (41.17 mmol) dimethyl tetrafluorosuccinate to a solution of 9.76 g (90,82 mmol) 5-amino-pentan-1-ol in 40 ml dry THF. After the exothermic reaction ceased, the reaction mixture was stirred for the duration of 4 h at room temperature. The solvent was distilled off, and the white crystalline residue was recrystallized from ethyl acetate/ethanol (1:1) and dried at 80 °C under vacuum. Yield: 12.73 g (86 %), m.p. 119 °C, elemental analysis for $C_{14}H_{24}F_4N_2O_4$ (360.4): calc. (found): C: 46.66 % (46.53 %), H: 6.71 % (6.50 %), N: 7.77 % (7.78 %), ^{1}H-NMR (acetone-d_6): δ (ppm) = 1.35-1.46 (m, 2H), 1.49-1.64 (m, 4H), 3.28-3.35 (m, 2H), 3.52-3.56 (t, 2H), 8.25 (s, 2H), ^{19}F-NMR (acetone-d_6): δ (ppm) = -118.05 (s), IR (KBr): 3295 cm^{-1} (N-H, O-H), 2940-2870 cm^{-1} (C-H), 1685 cm^{-1} (C=O), 1545 cm^{-1} (N-H), 1170-1130 cm^{-1} (C-F).

Subsequently, **1a** (n = 1) was obtained by reacting 3.61 g (10.0 mmol) N,N'-bis(5-hydroxypentyl)tetrafluorosuccinic diamide dissolved in 30 ml THF with 2.10 g (20.05 mmol) methacryloyl chloride in the presence of 2.20 g (21.7 mmol) triethylamine at 0 °C. The reaction was carried out under air. After stirring 45 h at room temperature, the solvent was removed at 35 °C under vacuum, bubbling traces of air through the mixture. The viscous residue was dissolved in methylene chloride, washed with 2N HCl, dried over Na_2SO_4, and recovered in vacuum as described above. Traces of air are required to prevent gelation! Yield: 4.57 g (92 %), m.p. 37-44 °C, ^{1}H-NMR (CD_3OD): δ (ppm) = 1.33-1.49 (m, 2H), 1.58-1.76 (m, 4H), 1.93 (s, 3H), 3.31-3.35 (m, 2H), 4.15-4.19 (t, 2H), 5.62 (s, 1H), 6.08 (s, 1H), ^{19}F-NMR ($CDCl_3$): δ (ppm) = -119.64 (s), IR (KBr): 1725 and 1695 cm^{-1} (C=O), 1640 cm^{-1} (C=C), 1550 cm^{-1} (N-H), 1180-1130 cm^{-1} (C-F), 940 cm^{-1} (=C-H), methacrylate conc.: calc. (found): 4.03 mol/kg (3.42 mol/kg).

The dimethacrylate **1b** (n = 2) was prepared accordingly. Yield: 96 %, m.p. 42-44 °C, ^{1}H-NMR (CD_3OD): δ (ppm) = 1.33-1.49 (m, 2H), 1.58-1.76 (m, 4H), 1.93 (s, 3H), 3.36-3.40 (m, 2H), 4.11-4.15 (t, 2H), 5.65 (s, 1H), 6.08 (s, 1H), ^{19}F-NMR ($CDCl_3$): δ (ppm) = -122.63 (s, 1F), -120.06 (s, 1F), IR (KBr): 1725 and 1695 cm^{-1} (C=O), 1640 cm^{-1} (C=C), 1555 cm^{-1} (N-H), 1190, 1170 and 1120 cm^{-1} (C-F), 940 cm^{-1} (=C-H), methacrylate conc.: calc. (found): 3.35 mol/kg (2.82 mol/kg).

The same procedure was applied for the preparation of **1c** (n = 3). Yield: 89 %, m.p. 61-79 °C, ^{1}H-NMR (CD_3OD): δ (ppm) = 1.33-1.49 (m, 2H), 1.58-1.76 (m, 4H), 1.93 (s, 3H), 3.36-3.40 (m, 2H), 4.11-4.15 (t, 2H), 5.56 (s, 1H), 6.08 (s, 1H), ^{19}F-NMR ($CDCl_3$): δ (ppm) = -122.74 (s, 1F), -121.89 (s, 1F), -119.94 (s, 1F), methacrylate conc.: calc. (found): 2.87 mol/kg (2.35 mol/kg).

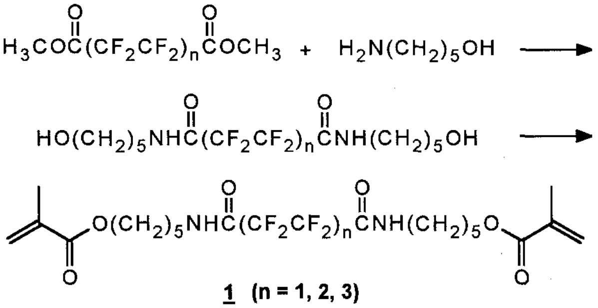
Preparation of the bis(2-methacryloyloxyethyl)oligo(tetrafluoroethene)s **2**: The fluorine-containing diesters were saponified with 85 % solution of KOH in water/ethanol(2:1). After acidification with conc. HCl the solvent was tripped off in vacuum and the resulting mixture of the fluorine-containing diacids and KCl was reacted with excess thionylchloride in the presence of few drops of DMF catalyst for the duration of 4 h under reflux. Dodecafluorosuberic acid chloride (82 % yield, b.p. 164-166 °C) and octafluoroadipic acid chloride (77 % yield, b.p. 129-130 °C) were isolated by distillation. The bis(2-methacryloyloxyethyl)dodecafluorosuberate **2b** (n = 3) was obtained by esterification of 2-hydroxyethyl methacrylate with dodecafluorosuberic acid chloride in the presence of pyridine: To a solution of 4.78 g (36.7 mmol) 2-hydroxyethyl methacrylate and 2.91 g (36.8 mmol) pyridine in 30 ml dry THF, cooled using an iced bath, 7.48 g (17.52 mmol) dodecafluorosuberic acid chloride were added. After stirring this mixture 16 h at room temperature, filtering off the salt, stripping off the solvent in vacuum, dissolving in methylene chloride, washing with aqueous 2N HCl, drying over sodium sulfate and removing methylene chloride, 9.45 g (88 %) of the viscous liquid **2b** (n = 3) was isolated.
Characterization: density at 20 °C: 1.4675 g/cm^3, n_D^{20} 1.4025, elemental analysis for $C_{20}H_{18}F_{12}O_8$ (614.3): calc. (found): C: 39.10 % (38.87 %), H: 2.95 % (2.96 %), ^{1}H-NMR (CDCl$_3$): δ (ppm) = 1.93 (s, 3H), 4.42-4.47 (t, 2H), 4.61-4.66 (t, 2H), 5.60 (s, 1H), 6.11 (s, 1H), ^{19}F-NMR (CDCl$_3$): δ (ppm) = -122.44 (s, 1F), -121.43 (s, 1F), -118.25 (s, 1F), IR (neat): 1785 and 1725 cm^{-1} (C=O), 1640 cm^{-1} (C=C), 1210 and 1150 cm^{-1} (C-F), 945 cm^{-1} (=C-H), methacrylate conc.: calc. (found): 3.26 mol/kg (3.22 mol/kg).

The dimethacrylate **2a** (n = 2) was prepared and characterized accordingly. Yield: 85 %, m.p. 27-29 °C, density at 20 °C: 1.4063 g/cm^3, n_D^{20} 1.4157, elemental analysis for $C_{18}H_{18}F_8O_8$ (514.3): calc. (found): C: 42.04 % (42.32 %), H: 3.52 % (3.65 %), ^{1}H-NMR (CDCl$_3$): δ (ppm) = 1.93 (s, 3H), 4.42-4.47 (t, 2H), 4.61-4.66 (t, 2H), 5.60 (s, 1H), 6.13 (s, 1H), ^{19}F-NMR (CDCl$_3$): δ (ppm) = -122.40 (s, 1F), -118.45 (s, 1F), IR (neat): 1785 and 1725 cm^{-1} (C=O), 1640 cm^{-1} (C=C), 1200-1170 cm^{-1} (C-F), 945 cm^{-1} (=C-H), methacrylate conc.: calc. (found): 3.89 mol/kg (3.85 mol/kg).

Photocrosslinking of the dimethacrylate-terminated oligo(tetrafluoroethene)s was performed as follows: A solution of 5.57 mg 2,2-dimethoxy-2-phenylacetophenone (Irgacure™ 651, obtained from Ciba-Geigy AG) in 1.15 g **2a** was poured into a mold (70mm·5mm·2mm), degassed, coverd with a thin glass plate and cured by irradiating it 180 s with UV light (320-350 nm, 250 mW/cm^2). The transparent test specimen was used for testing using a Rheometrics RSA II Solid Analyzer (1 Hz frequency, 10 K/min). The thermogravimetric analysis was performed on a Netzsch Thermal Analysis System STA 409 under nitrogen at 10 K/min. Solvent uptake was measured after immersing the 70 mm · 5 mm · 2 mm samples in solvents for the duration of 6 days at room temperature. The volume shrinkage after cure was determined by comparing the monomer and polymer densities.

Results and Discussion

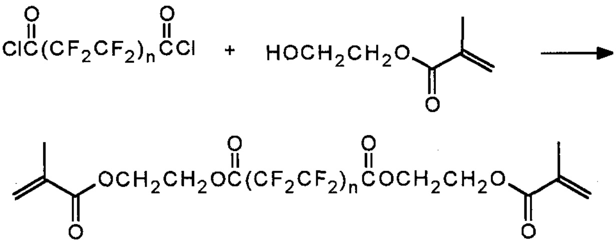
The dimethyl esters of dicarboxylic-acid-terminated oligo(tetrafluoroethene), obtained using Millauer's electrochemical telomerization process, proved to be versatile intermediates for the synthesis of dimethacrylates containing n=1, 2, 3 tetrafluoroethene units. Two strategies were successfully introduced to prepare two novel dimethacrylate monomer families. In the first synthetic strategy, as shown in Scheme 1, the diesters were reacted with 5-amino-pentan-1-ol to afford the N,N'-bis(5-aminopentyl)oligo(tetrafluoroethene)s in high yields. These dihydroxy-terminated oligo(tetrafluoroethene)s were then converted into the corresponding dimethacrylates (1a, 1b, 1c) by esterification with methacryloyl chloride in the presence of air. The 5-amino-pentan-1-ol was preferred over 2-amino-ethan-1-ol to circumvent cyclization reaction which could deplete the endgroup functionalities.



1 (n = 1, 2, 3)

Scheme 1 Preparation of the type 1 dimethacrylate-terminated oligo(tetrafluoroethene)s

In the second synthetic route, depicted in Scheme 2, the diester-terminated oligo(tetrafluoroethene)s were converted into the corresponding diacidchlorides which were esterified with 2-hydroxyethyl methacrylate. Also this route affords the dimethacrylate-terminated oligo(tetrafluoroethene)s of type 2 in high yields.



2 (n = 2, 3)

Scheme 2 Preparation of the type 2 dimethacrylate-terminated oligo(tetrafluoroethene)s

As is apparent from the monomer properties summarized in Table 1, the amide-containing dimethacrylates 1 melt at temperatures between 37 and 79 °C, whereas the dimethacrylates 2a, 2b are highly viscous liquids. In the series of 1a, 1b, 1c, the melt temperatures increase with increasing number of tetrafluoroethene units in the perfluoroalkylene segment.

Table 1 Properties of dimethacrylate-terminated oligo(tetrafluoroethene)s

Sample	n	R	m.p. [°C]	Functionalities [a] calc. [mol/kg]	Functionalities [a] found [mol/kg]
1a	1	$-O(CH_2)_5NH-$	37-44	4.03	3.42
1b	2	$-O(CH_2)_5NH-$	42-44	3.35	2.82
1c	3	$-O(CH_2)_5NH-$	61-79	2.87	2.35
2a	2	$-OCH_2CH_2O-$	27-29	3.89	3.85
2b	3	$-OCH_2CH_2O-$	< 0	3.26	3.22

a) methacrylate functionalities determined by ^{1}H-NMR end group analysis

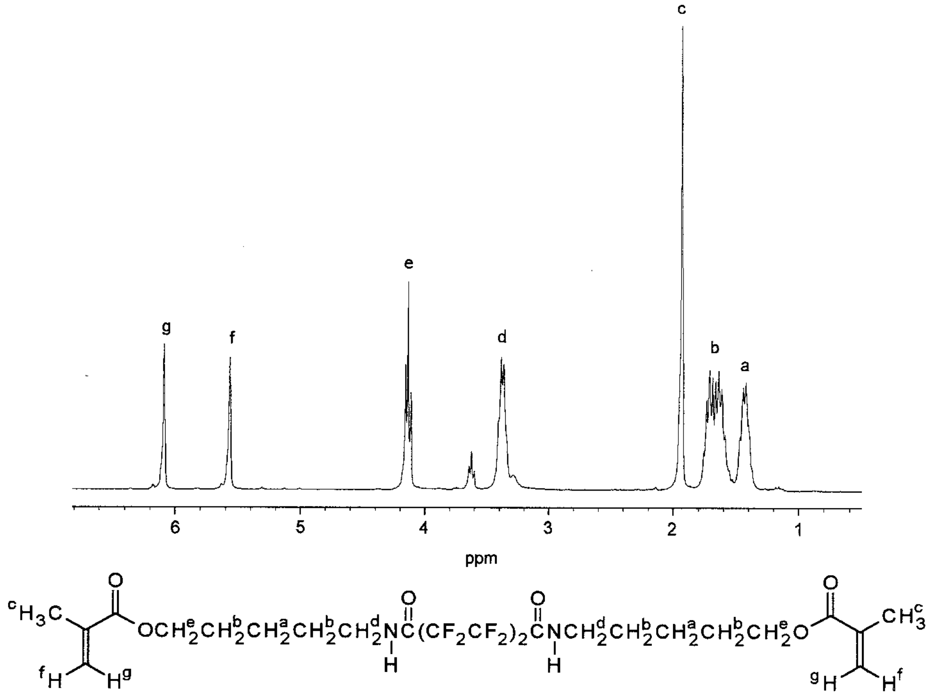


Figure 1 ^{1}H-NMR spectrum (300 MHz, $CDCl_3$) of 1b

In the case of both dimethacrylate families, high resultion ^{1}H-NMR spectroscopy has been applied as versatile tool to determine the methacrylate functionalities. Depicted in Fig. 1 is the ^{1}H-NMR spectrum of the N,N'-bis(5-methacryloyloxypentyl)octafluoroadipic diamide **1b**. The triplet at 3.65 ppm, located between the signals d ($C\underline{H}_2$-N) at 3.38 ppm and e ($C\underline{H}_2$-O-CO-) at 4.13 ppm, corresponds to the -$C\underline{H}_2$-OH of the non-reacted hydroxy endgroup of the diol precursor. Methacrylate functionalities calculated from the signal intensities of -$C\underline{H}_2$-O- versus -$C\underline{H}_2$-OH are summarized in Table 1 and vary between 82 and 85 % of the theoretical functionalities.

All methacrylates were found to undergo photocrosslinking when irradiated with UV light in the presence of the 2,2-dimethoxy-2-phenyl-acetophenone photoinitiator. Also in the case of crystalline monomers, which were cured in the molten state, the resulting polymers are amorphous. The glass transition temperatures were determined by dynamic mechanical analysis. For the 1-type dimethacrylates both the storage modulus E' (cf. Fig. 2) and the loss factor $\tan\delta$ (cf. Fig.3) were measured as a function of temperature. In contrast to the melting temperatures of the 1-type dimethacrylates in Table 1, the glass transition temperatures of the corresponding polymer networks, which are listed in Table 2, decrease with increasing the segment length of the oligo(tetrafluoroethene). This clearly reflects the influence of the increasing chain flexibility of the oligo(tetrafluoroethene) segment with increasing segment length. On the other hand, when the more flexible units were incorporated, the fluorine content increased and afforded higher thermal stabilities. In Table 2, the temperature at which 5 % weight loss was observed increased from 270 to 348 °C when one tetrafluoroethene unit was replaced by two tetrafluoroethene units. Only marginal changes were observed when three tetrafluoroethene units were incorporated.

Table 2 Properties of photocrosslinked dimethacrylate-terminated oligo(tetrafluoroethene)s

Monomer	n [a]	T_g [°C]	T_w [b] [°C]	shrinkage [%]	solvent swelling [%]	
					H_2O	toluene
1a	1	82	270	n.d. [c]	1.6	0.3
1b	2	74	348	n.d. [c]	1.2	0.6
1c	3	58	339	n.d. [c]	1.0	1.4
HEAMA [d]	-	138	327	11.0	2.2	0.6
2a	2	134	305	7.4	0.0	1.1
2b	3	91	309	7.3	0.0	2.2
2a/HEAMA		137	313	10.0	2.2	2.0

a) number of tetrafluoroethene units in the perfluoroalkylene segment
b) temperature at which 5 % weight loss occured
c) not determined d) bis(2-methacryloyloxyethyl)adipate

In Table 2 the 2a dimethacrylate was compared with the equivalent non-fluorine-containing dimethacrylate, the bis(2-methacryloyloxyethyl)adipate (HEAMA). Glass transition temperatures and thermal stabilities were similar, but the incorporation of the octafluorobutylene segments afforded much lower water-uptake and considerably lower volume shrinkage after cure. Blends of 2a and HEAMA gave performance similar to that of the pure HEAMA. This behavior could result from microphase separation processes or incomplete conversion of the methacrylates during cure. At present research is being directed towards the investigation of such hybrid networks.

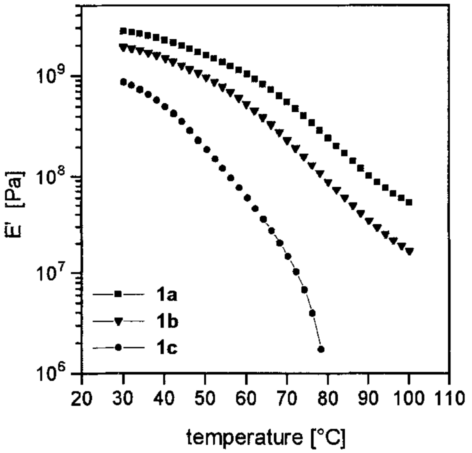


Figure 2 DMA analysis: storage modulus E' as a function of temperature

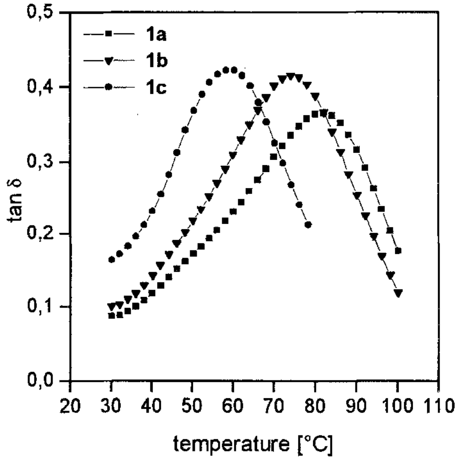


Figure 3 DMA analysis: loss factor tanδ as a function of temperature

Conclusion

Diester-terminated oligo(tetrafluoroethene)s, produced in an electrochemical tetrafluoroethene telomerization process, are versatile intermediates for the synthesis of thermoset resins containing well-defined oligo(tetrafluoroethene) segments. Either by esterification of the diacidchloride-terminated oligo(tetrafluoroethene)s with 2-hydroxyethyl methacrylate or by esterificaction of diol derivatives, prepared by reacting the diester with 5-amino-pentan-1-ol, dimethacrylate-terminated oligo(tetrafluoroethene)s are accessible in high yields. Such monomers are attractive thermoset resins which form highly crosslinked fluorine-containing polymers. Low water-uptake, higher flexibility, and low shrinkage are of interest in matrix resin applications, e.g. for applications as dental composites. For designing amphiphilic networks, such extraordinarily hydrophobic and oleophobic monomers could be incorporated into aliphatic or more hydrophilic networks to form micro- and nanophase-separated simultaneously interpenetrating networks.

Acknowledgement

The authors would like to thank Dr. H. Millauer for supplying us with diester-terminated oligo(tetrafluoroethene)-intermediates and Hoechst AG for sponsoring this research.

References

1) Plunkett RJ in Seymour RB, Kirshenbaum GS (eds.) "High Performance Polymers: Their Origin and Development", Elsevier Publ. Co.,Inc., New York 1986, p.261-266
2) Kotov S, Ivanov G, Kostov G (1988) J Fluor Chem 41: 293
3) Haszeldine RN (1951) Nature 167: 139
4) Millauer H (1988) DECHEMA Monogr 112: 429

Accepted January 22, 1994 C