Copolymerization of Acrylonitrile and Ethene in the Presence of Trifluoroacetic Acid as Complexing Agent

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ABSTRACT: The free radical copolymerization of ethene (ET) with acrylonitrile (AN) in the presence of carboxylic acids has been studied. Carboxylic acids and trifluoroacetic acid (TFA) in particular were found to be useful complexing agents for acrylonitrile with regard to the alternating copolymerization with ethene. The complexation via hydrogen bonding could be observed by IR analysis of the stretching frequency of the nitrile group in the monomer. The complex formation resulted in a decrease of the copolymerization parameter r_1 of the complexed and the uncomplexed comonomer acrylonitrile, which was found to decrease with increasing TFA/AN ratio. The degree of alternation could be increased by increasing the TFA/AN or the ET/AN ratio in the initial polymerization mixture. Almost strictly alternating copolymers were obtained with TFA as solvent. The copolymers showed high crystallinity and melting temperatures similar to the strictly alternating copolymer, which has been synthesized in the presence of $EtAlCl_2$ as a Lewis acid.

Introduction

The properties of linear copolymers are determined by their composition as well as the sequential arrangement of the monomers in the chain. In alternating copolymers the monomers are always linked together in the same regular fashion. It is quite obvious that the material properties differ from the random copolymers with the same monomer composition, as the new constitutional repeating unit is given by the two regularly linked comonomers. This is clearly demonstrated by the unusual properties of alternating copolymers of acrylics and olefins, such as the semicrystallinity of the alternating copolymers of ethene and acrylic comonomers, e.g. poly(acrylonitrile-*alt*-ethene), whereas the use of other electron donor monomers leads to amorphous polymers.[1]

Alternating copolymers are accessible by free radical polymerization, if the polarity difference of the two comonomers is large enough. This is expressed by the polarity terms *e* of the *e*−*Q* scheme of Alfrey and Price. Unfortunately, most conventional and readily available monomers are not sufficiently electron rich or electron poor to fulfill this condition. The acceptor properties of the electron poor monomer, such as acrylics, can be improved by complexation with Lewis acids, which decreases the electron density of the acceptor monomer, whereby homopolymerization is prevented and the addition of the electron rich donor monomer is accelerated.[2,3] This copolymerization has been often described to start spontaneously,[3] but this seems questionable in view of the unequivocally proven free radical initiation.[1,4−6] Exceptions might be the copolymerization of complexed acceptor monomers with styrene as electron donor comonomer, for which the initiation by an equimolar donor−acceptor complex between these monomers has been proposed.[7] Furthermore, it was suggested that this copolymerization is governed by the donor and acceptor character of the olefin.[8] However, no evidence for CT-complex formation has been found in the case of nonaromatic electron donor monomers.

The alternating copolymerization of complexed acrylic monomers with olefins has been reported by several authors. Ethylaluminum dichloride[1,2,4] and zinc chloride[5−10] are found to be suitable Lewis acids for acrylonitrile as acceptor monomer; Logothetis[11,12] demonstrated that alternating high-molecular-weight copolymers of acrylates and propylene can be prepared by using boron trifluoride as complexing agent.

Many Lewis acids have the disadvantage of being difficult to handle due to their air sensitivity, which makes their removal and recovery for further use after copolymerization almost impossible. Furthermore, the Lewis acids have to be used equimolar or even in excess in comparison to the acceptor monomer, which is often restricted by the poor solubility of the complexing agent in apolar organic solvents. In the case of the zinc chloride−diethyl ether complex and dichloromethane as solvent, it is possible to improve the solubility of the acrylic−$ZnCl_2$ complex by adding the Lewis base diethyl ether, which supports the compatibility of the Lewis acid to the solvent.[13,14] Furthermore, the workup of the copolymer is much easier than for, e.g., aluminum organyls as complexing agent, and the $ZnCl_2$ can be recovered almost quantitatively in a simple manner.[13]

In this paper we report on the influence of strong organic Brönsted acids, such as trifluoroacetic acid (TFA), on the copolymerization of acrylonitrile and ethene;[13] to the best of our knowledge, this is the first example which demonstrates that, besides the known Lewis acids, Brönsted acids are also suitable additives for the copolymerization of acrylics and olefins for generating alternating copolymers. Trifluoroacetic acid as complexing agent could be used in excess and even as a solvent, which allows very simple handling and removal from the reaction mixture after copolymerization and its recovery for further use.

Experimental Section

Materials. Acrylonitrile was refluxed with CaH_2 and distilled at atmospheric pressure. Ethene was obtained from Hoechst AG (>99.0%). Dichloromethane was refluxed from CaH_2 and distilled under an argon atmosphere. Trifluoroacetic acid was distilled under atmospheric pressure. Dicyclohexyl peroxydicarbonate (CHPC) as radical initiator was recrystallized twice from chloroform and methanol before use. Perfluorobutyroyl peroxide was prepared from perfluorobutyroyl chloride and hydrogen peroxide and was directly used in a solution of Freon-113 ($CF_2ClCFCl_2$), as described by Chengxue.[15]

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Table 1. Copolymerization of Acrylonitrile (AN) and Ethene (ET) without or in the Presence of Complexing Agents, Such as $ZnCl_2 \cdot Et_2O$ or Different Brönsted Acids, with CHPC as Radical Initiator at 40 °C in CH_2Cl_2 as Solvent $[AN]_0$ = 0.37 mol/L; $[ET]_0/[AN]_0$ = 10; time of polymerization, 15 h); an, et = Monomeric Units AN and ET in the Copolymer

no.	complexing acid (pK_s in H_2O)	$[acid]_0/[AN]_0$	AN conversion in mol %	M_n[a]	M_w[a]	an/et mole ratio in copolymer	degree of alternation[b]
1			4	5400	7000	2.17	0.46
2	$ZnCl_2 \cdot Et_2O$	1	58	25200	51000	1.59	0.63
3	CH_3SO_3H (−1.2)[c]	1	15	8100	10200	1.34	0.75
4	CF_3COOH (0.2)	1	17	9800	12600	1.25	0.80
5	CCl_3COOH (0.7)	1	15	8200	9300	1.45	0.69
6	$ClCH_2COOH$ (2.9)	1	13	7500	9800	1.65	0.61
7	HCOOH (3.7)	1	10	8000	10700	1.70	0.59
8	CH_3COOH (4.8)	1	10	7000	9400	1.70	0.59
9	CF_3COOH (0.2)[c]	6	18	8400	9800	1.13	0.88
10	CF_3COOH (0.2)[c,d]	35	22	8600	9900	1.02	0.98

[a] GPC analysis based on polystyrene calibration. [b] Mole ratio an−et/(an−et + an) of an−et and an sequences determined by ^{13}C-NMR analysis. [c] Copolymerization with perfluorobutyroyl peroxide as radical initiator at 20 °C. [d] Trifluoroacetic acid as solvent.

Copolymerization. Copolymerizations were run in batch in a 1 L glass pressure reactor that can withstand 12 atm. The following is a typical example.

A 100 mL aliquot of dichloromethane, 2.0 g (37 mmol) of acrylonitrile, 4.2 g (37 mmol) of trifluoroacetic acid, and 0.11 g (0.37 mmol) of CHPC were placed in a pressure reactor under nitrogen. The mixture was cooled to −80 °C, and 10.3 g (370 mmol) of ethene was added. The amount was measured by condensing the gas into a pressure tube, which was then attached to the reactor. The mixture was allowed to rise to room temperature and was heated at 40 °C for 15 h.

If trifluoroacetic acid was used in surplus in comparison to acrylonitrile, the analogous amount of perfluorobutyroyl peroxide was used as radical initiator, which allows the lower polymerization temperature of 20 °C at about the same initiator decomposition rate as CHPC at 40 °C.

After polymerization, all volatile compounds were removed in vacuum at room temperature. The copolymer was solved twice in hot acetone and precipitated in methanol. It was dried overnight in a vacuum oven at 50 °C. The yield of dried polymer was about 0.4 g.

Characterization. The copolymer composition was obtained by ^1H- and ^{13}C-NMR analysis using a Bruker AC 250 and DMSO-d^6 as solvent. Broad-band decoupling was used with a pulse width of about 45° and a pulse delay of 4 s.

Molar mass determination was done by gel permeation chromatography (GPC) with three Styragel columns (10^5, 10^4, 10^3 Å). GPC measurements were carried out at 60 °C in DMA as eluent at a flow rate of 1 mL/min. Polystyrene standards were used for calibration.

IR spectroscopic analysis was carried out with a FT-IR spectrometer Bio-Rad FTS-40. Differential scanning calorimetry (DSC) analysis was done with a Perkin-Elmer DSC 7. Calibration was carried out by using the melting points of indium and cyclohexane. The sample weight was between 5 and 10 mg and both heating and cooling rates were 20 K/min.

Results and Discussion

As has already been demonstrated, the complexation of the acceptor comonomer acrylonitrile (AN) with Lewis acids (i.e., $ZnCl_2 \cdot Et_2O$, $EtAlCl_2$) influences the comonomer reactivities and the copolymerization parameters.[1,8,10,12] Surprisingly, it was found that bipolymers with periodic comonomer sequences, ideally alternating copolymers of electron donor and acceptor comonomers, can be also synthesized in the presence of strong organic Brönsted acids.[13,16,17] This is reflected from the experimental and analytical data of a set of copolymerizations of ethene and acrylonitrile in the presence of different acids carried out at the same reaction conditions (Table 1, nos. 2−8). The effectiveness of the carboxylic acids with regard to the degree of et−an alternation increases with increasing acidity (nos. 3−8, Table 1). The best results could be obtained by using trifluoroacetic acid (TFA) as complexing agent, which could even be used as solvent for the copolymerization (no. 10; Table 1).

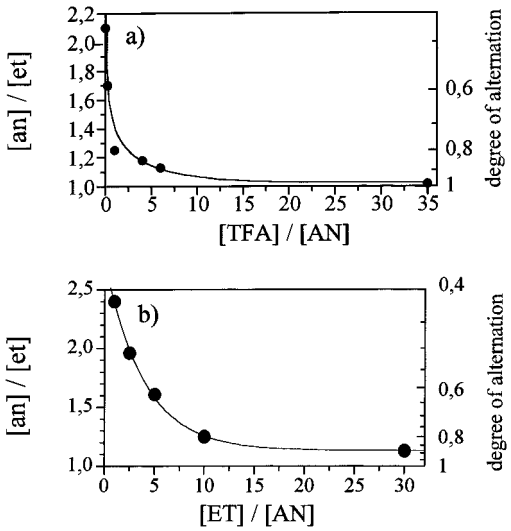


Figure 1. Dependence of the acrylonitrile (AN)/ethene (ET) mole ratio an/et in the copolymer obtained by free radical copolymerization in CH_2Cl_2 in the presence of trifluoroacetic acid (TFA) as complexing agent as a function of the TFA/AN mole ratio ((a) mole ratio in the feed ET/AN = 10) and as a function of the ET/AN mole ratio in the initial polymerization mixture ((b) mole ratio TFA/AN = 1).

The 1:1 copolymer composition of the alternating structure could be approached by increasing the TFA/AN mole ratio in the initial polymerization mixture. As can be seen in Figure 1a, strictly alternating copolymers of ethene (ET) and acrylonitrile (AN) could be obtained by using TFA as solvent, where it exists in a 35-fold excess in comparison to acrylonitrile.

Of course, given a certain TFA/AN mole ratio, the degree of alternation can also be increased by charging more ethene to the copolymerization mixture, which takes advantage of the common variation of copolymer composition by the comonomer feed ratio. However, it has to be clearly stated that only alternating an−et sequences, which may be interrupted by short an polyades (deviation from the strict alternation) and absolutely no et sequences are formed under the given polymerization conditions; contrarily, the acid-free AN−ET copolymerization at elevated pressure leads to copolymers, where both longer an and et sequences occur (cf. refs 17 and 18).

The reason for the unexpected effect of carboxylic acids and TFA in particular is attributed to both the

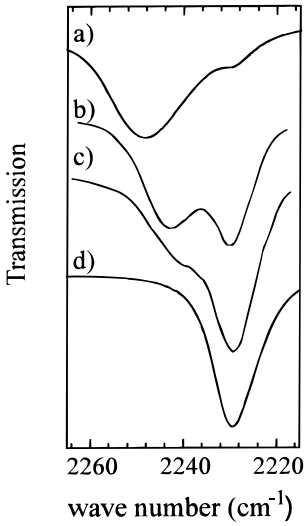


Figure 2. IR spectra of the range of the nitrile stretching frequency of acrylonitrile in the presence of equimolar amounts of trifluoroacetic acid (a), formic acid (b), and acetic acid (c), and pure acrylonitrile (d).

nitrile−acid interaction and a hydrogen-bonded clustering of the acids around the propagating site. The effect of the complexation of the nitrile group with TFA on both the reactivity of the AN free radical and the electron density of the double bond of the AN monomer has to considered as well: Similar to Lewis acid complexation (cf. ref 13), the TFA complexation enhances the reactivity of the complexed AN radical chain end toward the olefin comonomer, and vice versa favors the addition of the complexed AN monomer toward the ET radical chain end.

The molecular interaction between the nitrile group and the carboxylic acid was shown by IR spectra of the complexed acrylonitrile. The stretching frequency of the uncomplexed (ca. 2230 cm^{-1}) as well as the complexed nitrile group (at higher wavenumbers) could be detected. It was found that the complexing tendency increases with increasing strength of the carboxylic acid, as reflected from the increase in the ratio of the absorption bands of the complexed to the uncomplexed nitrile (Figure 2).

The stronger hydrogen accepting properties of the nitrile group compared to the carboxylic group of the complexing acid leads to an equilibrium of acid-complexed nitrile groups and acid dimers; the preferred formation of hydrogen-bonded cyclic dimers in apolar media is disrupted when the polarity and/or the concentration of polar components in the medium increaes (cf. ref 18). This may result in the formation of a cluster of hydrogen-bonded acid molecules at the nitrile groups of the monomer and the polymer chain, which could lead to the steric inhibition of the acrylonitrile addition to the polymer chain (Figure 3). Obviously, the addition of the much smaller uncomplexed olefin to the polymer chain is not inhibited. In agreement with this assumption, it could be shown that the radical homopolymerization of acrylonitrile is inhibited dramatically in the presence of TFA as complexing agent.

The alternating structure is demonstrated by ^{13}C-NMR analysis of the nitrile groups of the copolymers (Figure 4). The strictly alternating copolymer contains no et−an−an triads as defect structures (curve 5, Figure 4). The et−an−an triad content increases with increasing an/et ratio in the copolymer and an−an−an triads are only observed for an/et mole ratios higher than about 1.3 (see curve 3, Figure 4). The copolymer obtained in TFA as solvent is almost free of any an−an diads, thus proving the high efficiency of TFA for the alternating copolymerization.

The determination of the an/et mole ratio in the copolymer can be carried out by ^{1}H- or ^{13}C-NMR spectroscopy. In the former case, the signals of the initiator (cyclohexyl from dicyclohexyl peroxydicarbonate) cannot be separated from the copolymer methylene signals. This is illustrated in Figure 5, where the ^{1}H-NMR spectra of copolymers of ethene and acrylonitrile with similar an/et mole ratios and different initiator end groups (cyclohexyl or perfluorobutyroyl) are compared. Consequently, the ethene content determined by ^{1}H-NMR analysis is too high. In contrast to this, the ^{13}C-NMR spectroscopic determination is much more accurate, since the nitrile-C signals of the et−an−et, et−an−an, and an−an−an triads, which depend on their configurational environment, are well separated, as seen in Figure 4. The integration of the different signals allows the determination of the an/et ratio of the

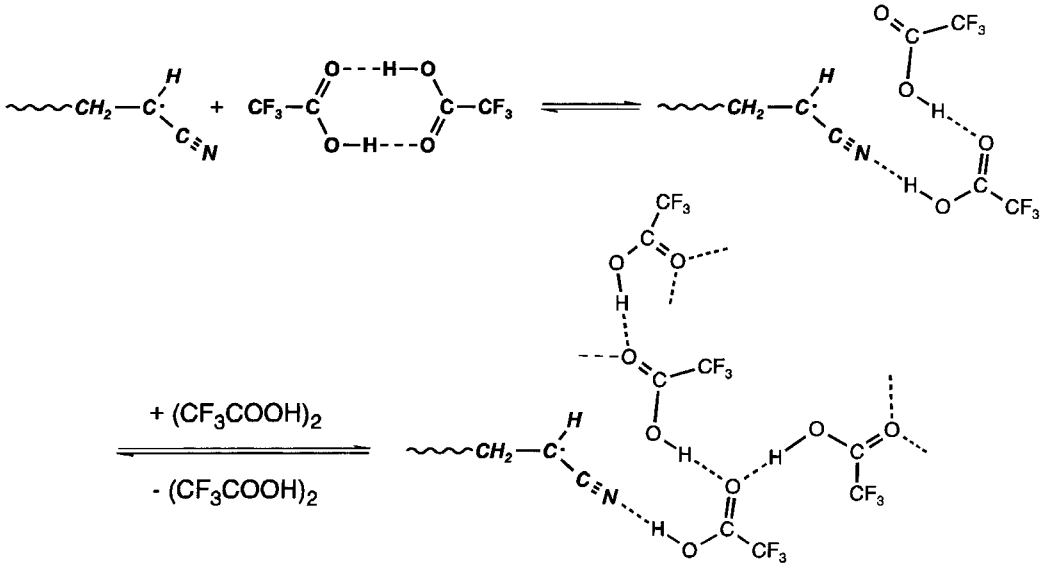


Figure 3. Equilibrium of complexed acrylonitrile and dimers of trifluoroacetic acid and model for the formation of clusters of hydrogen-bonded acid molecules at the nitrile groups.

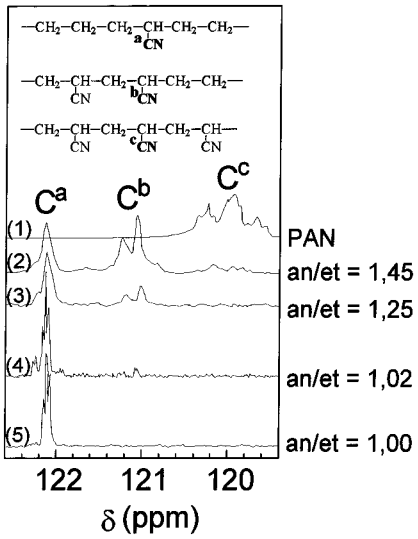


Figure 4. ^{13}C-NMR spectra (CN region; in DMSO-d_6; 75 MHz) of poly(acrylonitrile) (PAN; curve 1) and the ethene (ET)/acrylonitrile (AN) copolymers with different an/et comonomer compositions, as obtained by free radical polymerization of ET and AN in CH_2Cl_2 solvent in the presence of trifluoroacetic acid (TFA) at various mole ratios TFA/AN in the initial polymerization mixture; (curve 2) TFA/AN = 0.25; (curve 3) TFA/AN = 1; (curve 4) pure TFA−solvent; (curve 5) strictly alternating ET−AN copolymer as obtained with $EtAlCl_2$ complexation (cf. ref 1).

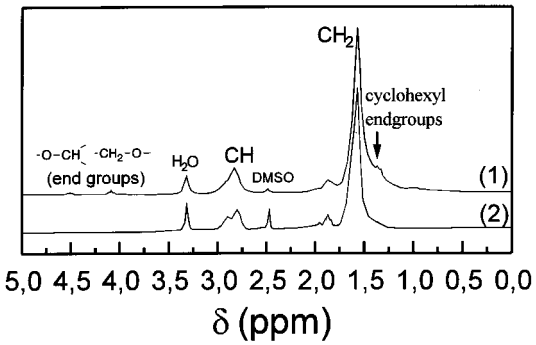


Figure 5. ^{1}H-NMR spectra of copolymers of ethene (ET) and acrylonitrile (AN) with similar built-in an/et contents (an/et ∼ 1.25) synthesized by free radical polymerization in the presence of trifluoroacetic acid (TFA) in CH_2Cl_2: (curve 1) dicyclohexyl peroxydicarbonate initiator (polymerization temperature: 40 °C) and mole ratio TFA/AN = 1 and ET/AN = 10 in the initial polymerization mixture; (curve 2) perfluorobutyroyl peroxide initiator (polymerization temperature: 20 °C) and mole ratio TFA/AN = 1 and ET/AN = 10 in the initial polymerization mixture.

copolymer by using the following equation:

$$\text{an/et} = (a + b + c)/(a + b/2)$$

where a, b, and c are the integrals of alternating sequences (et−an−et) (a), et−an−an triads (b), and an−an−an triads (c), determined by high-resolution ^{13}C-NMR spectroscopy. This method can be used in spite of the NOEs, which normally do not allow the integration, because of the small differences in the chemical shifts. The above comparison illustrates that ^{13}C-NMR is the preferred method for compositional analysis of these copolymers.

The influence of TFA on the copolymerization of ethene and acrylonitrile could be quantified by the graphical determination of the copolymerization parameters after Fineman−Ross (Figure 6). The r_2 parameter of the comonomer ethene was assumed to be zero, as

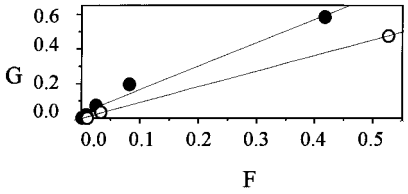


Figure 6. Graphical evaluation of linear copolymerization equations after Fineman−Ross for the free radical copolymerization of acrylonitrile (AN, M_1) and ethene (M_2) at 40 °C in CH_2Cl_2 in the presence of trifluoroacetic acid (TFA): (○) mole ratio TFA/AN = 1 in the initial polymerization mixture; (●) TFA without another solvent (mole ratio TFA/AN = 35). $F = ([M_1]^2 m_2)/([M_2]^2 m_1)$ and $G = ([M_1]/[M_2])(1 - m_2/m_1)$ with $[M_1]$ and $[M_2]$ = charged comonomer concentration in the copolymerization and $m_{1,2}$ = built-in comonomer.

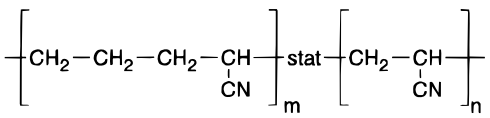
Table 2. Copolymer Composition et/an (Mole Ratio of Built-in Ethene and Acrylonitrile Units) and Comonomer Mole Ratio ET/AN in the Feed in the Radical Copolymerization of Ethene (ET) and Acrylonitrile (AN) at 40 °C in CH_2Cl_2 in the Presence of Trifluoroacetic Acid (TFA) for Two Different Mole Ratios TFA/AN and Corresponding Copolymerization Parameter r_1 (Index 1 Denotes AN)

	TFA/AN = 1					TFA/AN = 35		
ET/AN	1.0	2.5	5.0	10	30	1.0	5.0	10
et/an[a]	0.42	0.51	0.62	0.80	0.88	0.53	0.82	0.98
r_1[b]			1.35				0.9	

[a] Determined by ^{13}C-NMR analysis (see text). [b] Determined after Fineman−Ross (see Figure 6 and text).

ET homopolymerization or even the formation of et−et diads does not occur at these copolymerization conditions.[6] Table 2 shows the decrease of the copolymerization parameter r_1 of acrylonitrile upon addition of an excess of TFA, where r_1 is significantly lower than in the case of an equimolar AN/TFA ratio in the initial polymerization mixture. If the ^{1}H-NMR-determined composition of the copolymer is taken as a basis for the calculation of the copolymerization parameter r_1, the values are much too low, as explained above (e.g., for an equimolar TFA/AN mole ratio: $r_1 = 0.7$).

The copolymers containing an excess of acrylonitrile (an/et mole ratio > 1) can be correctly described as random copolymers, where the repeating units are given by cyanobutene (crystallizable alternating an−et sequences) and cyanoethene (surplus an sequences, which inhibit the crystallization):[4,13]



Consequently, the melting temperature and the corresponding melting endotherm are lowered by increasing the acrylonitrile content in the copolymer, as shown by the DSC traces in Figure 7. Simultaneously, the glass transition temperature increases with increasing an/et composition from T_g = 281 K (an/et = 1.02; curve 2) to T_g = 290 K (an/et = 1.25; curve 3). Since the molar masses of the copolymers (curves 2 and 3) are in the same range (see nos. 10 and 4, Table 1), this difference in T_g is only related to compositional changes. The highest melting temperature (T_m = 438 K) and crystallinity could be obtained by free radical copolymerization in the presence of ethylaluminum dichloride (EADC) (Figure 7, curve 1), which leads to strictly alternating copolymers of ethene and acrylonitrile, as already

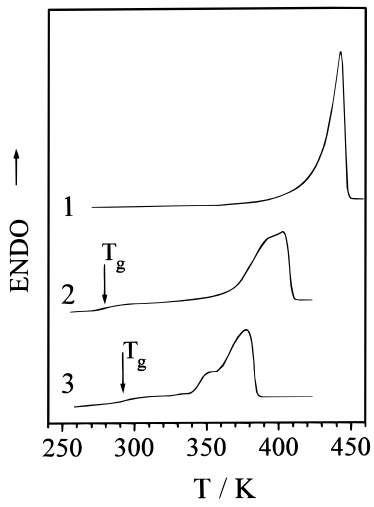


Figure 7. DSC curves of poly(ethene-*alt*-acrylonitrile) obtained by free radical copolymerization in the presence of ethylaluminum dichloride in CH_2Cl_2 at −78 °C (curve 1),[1] of almost strictly alternating ET−AN copolymer obtained by free radical copolymerization at 20 °C in TFA as solvent (mole ratio TFA/AN = 35) (curve 2), and poly(4-cyanotetramethene-*stat*-acrylonitrile) (curve 3, copolymer composition an/et = 1.25) obtained by free radical polymerization in CH_2Cl_2 at 40 °C in the presence of TFA (employed mole ratio TFA/AN = 1).

demonstrated.[1,4] A slight deviation from the strictly alternating structure (see no. 10, Table 1 and Figure 4, curve 4) results in melting temperature depression, as reflected from $T_m = 403$ K of the copolymer synthesized in TFA solvent (Figure 7, curve 2), and the copolymer with 20 mol % an−an diads and 80 mol % et−an sequences (see no. 4, Table 1 and Figure 4, curve 3) exhibits a melting endotherm at 381 K. In this context, it should be noted that copolymers synthesized by $ZnCl_2 \cdot Et_2O$[6,13] showed a much lower crystallinity than the analogous copolymers with the same degree of alternation but obtained in the presence of TFA. The reason for this unusual behavior is still obscure, since no or only minor differences in the tacticity of the copolymers were observed. It might be that the microstructure of the polymer chain with regard to the average an−et sequence length and the resulting differences in crystallite size becomes effective, which could be related to the composition of the polymerization mixture and the copolymerization conditions.

Conclusion

Summing up, the method with TFA as complexing agent simplifies the handling of the copolymerization. The solvent and the complexing agent can be readily removed from the reaction mixture after copolymerization; it also allows their recovery for further use. Furthermore, the complete exclusion of water during polymerization is—contrary to EADC as complexing agent—no longer necessary. The synthesized copolymers showed high crystallinity and melting temperatures similar to those prepared in the presence of EADC. Thus, carboxylic acids, and trifluoroacetic acid in particular, are suitable additives in radical copolymerization of acrylics and olefins and a feasible route to such copolymers with periodic sequences.

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