Available online at www.sciencedirect.com
ScienceDirect
Mendeleev Commun., 2023, **33**, 568–571

Mendeleev Communications

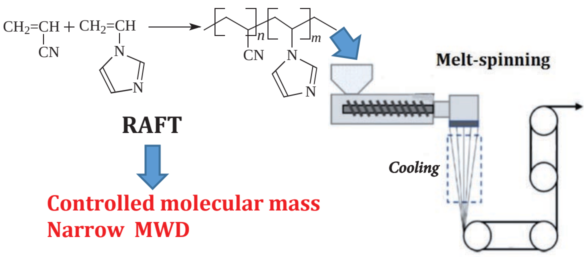
Synthesis and thermal behavior of RAFT-based copolymers of acrylonitrile and 1-vinylimidazole

Natalia I. Osipova,[a] Anna V. Plutalova,[a] Roman V. Toms,*[b] Nikolay I. Prokopov[b] and Elena V. Chernikova*[a]

[a] *Department of Chemistry, M. V. Lomonosov Moscow State University, 119991 Moscow, Russian Federation. E-mail: chernikova_elena@mail.ru*
[b] *M. V. Lomonosov Institute of Fine Chemical Technologies, MIREA – Russian Technological University, 119571 Moscow, Russian Federation. E-mail: toms.roman@gmail.com*

DOI: 10.1016/j.mencom.2023.06.041

The copolymers of acrylonitrile and 1-vinylimidazole with a narrow molecular weight distribution (MWD) were synthesized for the first time by the reversible addition–fragmentation chain transfer (RAFT) polymerization in a DMSO solution in the presence of acetic acid. Their thermal behavior difference upon heating in argon and in air along with ability to melt make them promising precursors for carbon fiber production.



Keywords: reversible addition–fragmentation chain transfer polymerization, acrylonitrile copolymers, 1-vinylimidazole, cyclization, thermo-oxidative stabilization, melt spinning.

Melt spinning is widely used for production of polymer fibers.[1] Its main advantage over spinning from solution[2] is the environmental friendliness due to the absence of organic solvents. However, it cannot be applied to traditional acrylonitrile (AN) copolymers that undergo cyclization reaction upon heating before melting. To solve this problem, researchers usually increase the amount of a comonomer up to 10–25 wt%, decrease the molecular weight (MW) of a copolymer below 50 kDa and/or add a plasticizer up to 20–30 wt%.[3–5] Alkyl (meth)acrylates or vinyl acetate are commonly used as comonomers.[6] However, the further transformation of melt-spun precursors into carbon fibers is complicated by the melting of the precursor. To overcome this problem, it was suggested that 1-vinylimidazole (VIM) be used as a comonomer. In this case, the melt temperature of the copolymer in inert atmosphere is below the onset temperature of the cyclization, while in air the thermo-oxidative reactions proceed before copolymer melting, providing the route for production of carbon fiber.[7,8]

Recently, we have described the synthesis of the AN–VIM copolymers by conventional radical copolymerization in a DMSO solution and have studied the thermal behavior of the copolymers upon heating in argon and in air.[9] The published data and our results suggested that copolymers containing ~20 mol% of VIM would be able to melt. However, these copolymers have a relatively broad molecular weight distribution (MWD), which restricts the melt stability. Our attempt to solve this problem through reversible addition–fragmentation chain transfer (RAFT) copolymerization in a DMSO solution resulted in a low yield (below 15%) of the copolymer, but in a good control of the MWD. In the present research we succeeded in the controlled synthesis of AN–VIM copolymers with a moderate yield (up to ~40%) and explored their thermal behavior.

The AN–VIM copolymers were synthesized by RAFT polymerization in a DMSO solution in the presence of acetic acid.[†] The total monomer conversion was determined by gravimetry. As was shown earlier,[10] acetic acid is able to accelerate RAFT homopolymerization of VIM. Thus, it was used in RAFT copolymerization of AN and VIM, aiming at a higher copolymer yield. Table 1 displays the influence of acetic acid on conversion, composition[‡] and MWD of RAFT-based copolymers. As can be seen, an increase in the VIM molar content results in a higher yield of the copolymer, a decrease in the MW and a narrowing of the MWD. Thus, a 5-fold molar excess of acetic acid with respect to VIM is enough to produce

Table 1 Molecular characteristics of RAFT-based AN–VIM copolymers synthesized in the presence of acetic acid. The molar ratio AN/VIM = 4 : 1, 60 wt% of DMSO, $C_{\mathrm{CPDTC}} = 5 \times 10^{-3}$ mol dm^{-3}, $C_{\mathrm{AIBN}} = 10^{-3}$ mol dm^{-3}, T = 80 °C, and time 24 h.

Copolymer	VIM/acetic acid	Conversion (%)	M_n/kDa	$Đ$	VIM molar fraction F_{VIM}/mol%
C1	1 : 0.5	6.2	71.7	2.9	19.7
C2	1 : 1	37.4	54.6	2.4	20.6
C3	1 : 2	41.9	22.2	2.2	21.6
C4	1 : 5	42.4	11.7	1.22	15.1

[†] Copolymers of AN and VIM were synthesized as follows. The RAFT agent, namely dibenzyl trithiocarbonate [BTC, BnSC(=S)SBn, 97%] or 2-cyano-2-propyl(dodecyl)trithiocarbonate [CPDTC, $\mathrm{Me_2(CN)CSC(=S)SC_{12}H_{25}}$, 97%], and azobis(isobutironitrile) (AIBN) were dissolved in the mixture of monomers taken in the molar ratio AN/VIM = 4 : 1 and DMSO (60 wt% with respect to monomers). Glacial acetic acid was added in the molar ratio VIM/acetic acid = 1 : 5, 1 : 2, 1 : 1 and 1 : 0.5. The reaction mixture was polymerized under nitrogen atmosphere at 80 °C.

[‡] The copolymer composition was determined by ATR FTIR spectroscopy. The calibration curve was obtained from the mixtures of the monomers of the known molar ratio; the intensities ratio of the characteristic bands assigned to $\nu_{\mathrm{C-N=}}$ = 665 cm^{-1} (VIM) and ν_{CN} = = 2229 cm^{-1} (AN) was used.[9]

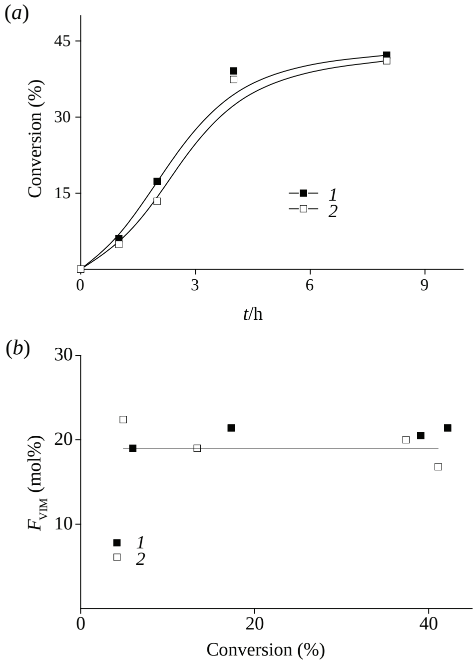


Figure 1 Dependence of (*a*) monomer conversion on the copolymerization time and (*b*) VIM molar fraction in the copolymer on the monomer conversion. The molar ratio AN/VIM = 4 : 1, 60 wt% of DMSO, $C_{\mathrm{BTC}} = C_{\mathrm{CPDTC}} = 5 \times 10^{-3}$ mol dm^{-3}, $C_{\mathrm{AIBN}} = 10^{-3}$ mol dm^{-3}, and $T = 80$ °C. RAFT agent: (*1*) BTC and (*2*) CPDTC.

the copolymer with an appropriate yield and controlled MW and MWD. So, in further experiments the molar ratio VIM/acetic acid = 1 : 5 was used.

Figure 1(*a*) presents the kinetics of RAFT copolymerization of AN and VIM in a DMSO solution in the presence of acetic acid taken in 5a-fold excess with respect to VIM. The dependence of the monomer conversion on the polymerization time has an S-shape, which is typical for RAFT polymerization, and is similar for both trithiocarbonates, thus confirming that the both leaving groups are efficient in the reinitiation of polymerization.[11] According to our previous data, VIM is a less active monomer in copolymerization with AN and the monomer reactivity ratio in DMSO is $r_{\mathrm{VIM}} = 0.22$ and $r_{\mathrm{AN}} = 0.88$.[9] The copolymer composition (F_{VIM}) remains roughly constant throughout the copolymerization providing the compositional homogeneity of the formed copolymers [Figure 1(*b*)]. The experimental values of F_{VIM} are in accordance with the theoretical value [solid line, Figure 1(*b*)] calculated on the basis of the monomer reactivity ratio confirming that the addition of acetic acid has no visible effect on the relative monomer activity.

To confirm the validity of the RAFT copolymerization mechanism, the MWD of the formed copolymers was analyzed using size exclusion chromatography (SEC).[§] Figure 2 displays MWDs of the copolymers synthesized using CPDTC [Figure 2(*a*)] and BTC [Figure 2(*b*)]. As is seen, the MWDs of the copolymers synthesized in the presence of CPDTC shift to the high-molar mass region throughout monomer conversion. The conversion transformation of the MWD of the copolymers synthesized in the presence of BTC is negligible. However, their MWDs are noticeably narrower than the MWD of the copolymer synthesized in conditions of conventional free radical copolymerization.

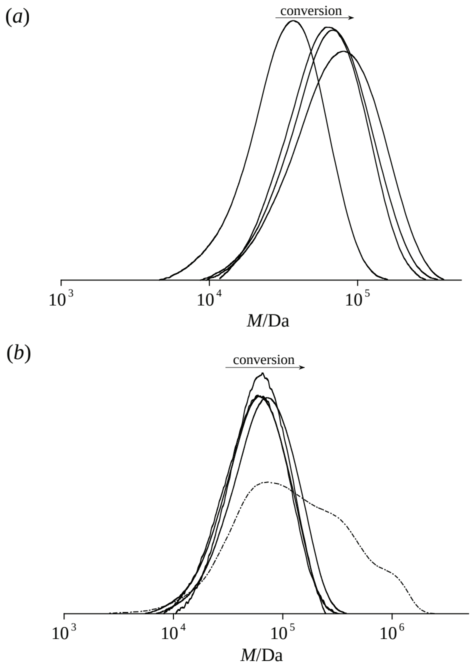


Figure 2 SEC curves normalized by the unit area for the polymers formed at various monomer conversions during copolymerization of AN and VIM mediated by (*a*) CPDTC and (*b*) BTC. The molar ratio AN/VIM = 4 : 1, 60 wt% of DMSO, $C_{\mathrm{BTC}} = C_{\mathrm{CPDTC}} = 5 \times 10^{-3}$ mol dm^{-3}, $C_{\mathrm{AIBN}} = 10^{-3}$ mol dm^{-3}, and $T = 80$ °C. The dash dot curve corresponds to the copolymer obtained in the absence of BTC.

The copolymers formed are ‘living’ and their number average molar mass (M_{n}) increases with progress in monomer conversion [see Figure 3(*a*)]. The different slopes of the M_{n} *vs.* conversion plots indicate a different efficiency of RAFT agents in copolymerization.[11] The dispersity ($Đ = M_{\mathrm{w}}/M_{\mathrm{n}}$) is lower than that obtained in conventional copolymerization ($Đ = 4.2$) and lies in the range 1.4–1.6 [Figure 3(*b*)]. The low difference between AIBN and RAFT agent concentrations is responsible for relatively high values of *Đ* for RAFT-based copolymers.

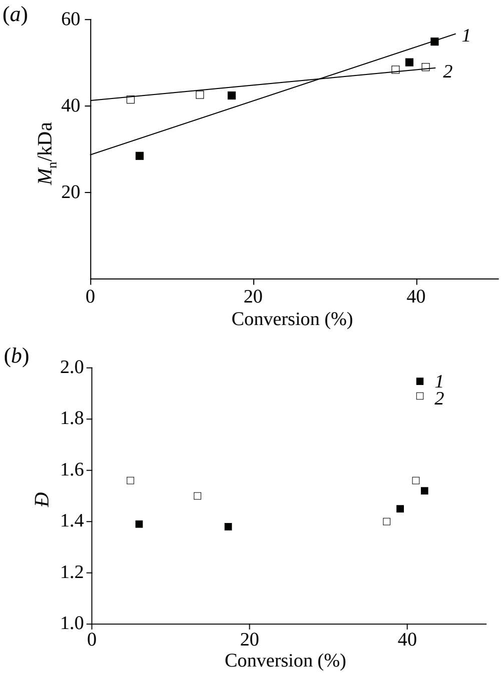


Figure 3 Dependences of (*a*) M_{n} and (*b*) dispersity *Đ* on the monomer conversion for copolymers formed during copolymerization of AN and VIM mediated by (*1*) CPDTC and (*2*) BTC . The molar ratio AN/VIM = 4 : 1, 60 wt% of DMSO, $C_{\mathrm{BTC}} = C_{\mathrm{CPDTC}} = 5 \times 10^{-3}$ mol dm^{-3}, $C_{\mathrm{AIBN}} = 10^{-3}$ mol dm^{-3}, and $T = 80$ °C.

[§] The measurements were performed in DMF containing 0.1 wt% of LiBr at 50 °C using a PolymerLabs GPC-120 chromatograph equipped with a refractive index detector and two PLgel 5 μm MIXED-B columns for the molecular mass range from 5×10^2 to 1×10^7 g mol^{-1}. The SEC system was calibrated using narrow-dispersed linear poly(methyl methacrylate) (PMMA) standards.

Table 2 Characteristics of RAFT-based AN–VIM copolymers . The molar ratio AN/VIM = 4 : 1, 60 wt% of DMSO, the molar ratio RAFT agent/AIBN = 5, T = 80 °C, and time 8 h. The molar ratio VIM/acetic acid = 1 : 5.

Copolymer	RAFT agent	Conversion (%)	M_n/kDa	$Đ$	F_{VIM} (mol%)
C5	CPDTC	42.2	48.9	1.38	21.4
C6	BTC	41.1	48.4	1.40	16.8

To investigate the influence of the characteristics of the polymers on their thermal behavior, samples C1–C4 (Table 1) and C5, C6 (Table 2) were used. These samples are synthesized using various amounts of acetic acid and various RAFT agents and differ by their MW and composition.

Table 3 Analysis of DSC thermograms registered in inert atmosphere for C1–C6 copolymers.

Copolymer	F_{VIM} (mol%)	T_p/°C	$-\Delta H$/J g^{-1}	E_a/kJ mol^{-1}
C1	19.7	175 327	−31 103	–
C2	20.6	172 322	−58 249	117 ± 14
C3	21.6	160 328	−37 178	129 ± 19
C4	15.1	324	632	–
C5	21.4	161 320	−40 168	108 ± 8
C6	16.8	310	121	109 ± 16

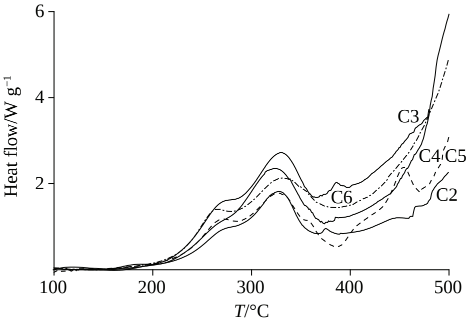


Figure 5 DSC thermograms of copolymers C2–C6 recorded at 10 K min^{-1} in air.

Figure 4 displays the DSC[¶] thermograms of copolymers C1–C4 [Figure 4(*a*)] and C5, C6 [Figure 4(*b*)] registered under argon in dynamic conditions (10 K min^{-1}). The shape of the thermogram depends on the copolymer composition. An endothermic peak is observed on the thermogram in the range of 110–210 °C referring to copolymer melting if F_{VIM} is above 19 mol% (C1–C3, C5). Below this value, the copolymer melting is masked by the cyclization reaction of nitrile groups.[9] The temperatures (T_p) of the maximum (exothermic) and minimum (endothermic) of the heat flow as well as the enthalpy of the corresponding processes are summarized in Table 3. The T_p values are relatively close due to the low difference in the copolymer composition, and they are insensitive to the MW of the copolymers. The activation energy of cyclization was estimated from the thermograms of copolymers C2, C3, C5 and C6 recorded at various ramp rates. Processing of the data by equation (1)[12]

$$-\frac{E_a}{R} = \frac{d\left[\ln\left(\frac{\varphi}{T_p^2}\right)\right]}{d\left(\frac{1}{T_p}\right)}, \qquad (1)$$

where R is the universal gas constant, T_p is the peak temperature (K), and φ is the heating rate (K min^{-1}), results in the linear dependences of $\ln\left(\varphi/T_p^2\right)$ on $1/T_p$. The values of activation energy of the cyclization reaction calculated from these data are summarized in Table 3. As can be seen, these values are similar taking into account the gaps of the experiment and the average value of the cyclization activation energy is 116 ± 14 kJ mol^{-1}. The data obtained in the present work compared with that obtained for copolymers synthesized through conventional copolymerization[9] suggest that the RAFT mechanism (the presence of the RAFT agent residues in macromolecules and narrow MWD) have no impact on the mechanism of the cyclization reaction.

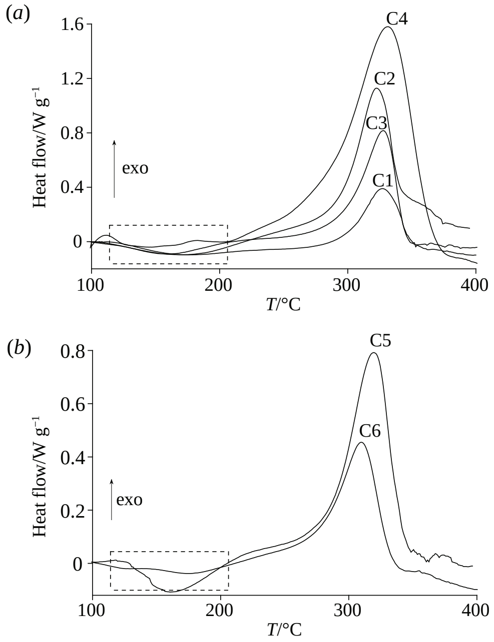


Figure 4 DSC thermograms of copolymers (*a*) C1–C4 and (*b*) C5, C6. The heating rate is 10 K min^{-1} under argon.

Upon heating in air, several new reactions such as oxidation and dehydration proceed along with cyclization of nitrile groups, resulting in the shift of exothermic peaks to a low-temperature region (Figure 5). Thermograms of the studied copolymers are similar as well as the T_p and ΔH values (Table 4), and no visible effect of the RAFT mechanism on the thermal behavior of the AN–VIM copolymers can be detected.

Thus, we have shown that AN–VIM copolymers exhibit a similar thermal behavior in argon (cyclization) and in air (oxidation, dehydration, cyclization) independently of their MW and MWD. However, the copolymer composition in contrast to the MW (M_n = 11.7 71.7 kDa) affect the melting ability of the copolymers. This important result allows simplification of the melt-spinable AN–VIM copolymer preparation by the use of a conventional chain transfer agent. The synthesis in the presence of 1 mol% of 2-mercaptoethanol resulted in the formation of the copolymer (M_n = 36.9 kDa, $Đ$ = 2.1) with a similar thermal behavior (Figure 6) as described above.

Table 4 Analysis of DSC thermograms registered in air for C2–C6 copolymers.

Copolymer	F_{VIM} (mol%)	T_p/°C	$-\Delta H$/J g^{-1}
C2	20.6	269, 327	507
C3	21.6	268, 330	615
C4	15.1	262, 324	683
C5	21.4	272, 326	727
C6	16.8	266, 331	614

[¶] Differential scanning calorimetry was performed on a Netzsch DSC 204 (Germany) in the atmosphere of a dry gas (air, argon) at a flow rate of 100 ml min^{-1} in the range of 30–500 °C and a heating rate from 5 to 30 K min^{-1} in air and 10 K min^{-1} in argon.

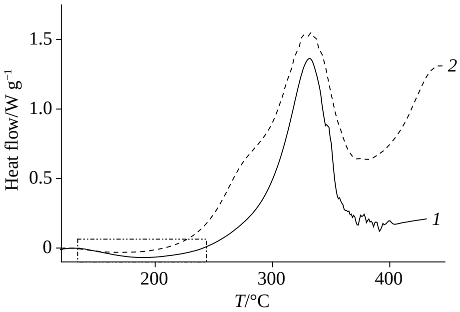


Figure 6 DSC thermogram of the copolymer synthesized in the presence of 2-mercaptoethanol recorded at 10 K min^{-1} in (*1*) argon and (*2*) air.

In summary, it can be concluded that the copolymers of acrylonitrile and 1-vinyl imidazole with a narrow molecular weight distribution synthesized in DMSO containing about 20 mol % of VIM are promising for the melt-processing technique.

References

1 R. Hufenus, Y. Yan, M. Daune and T. Kikutani, *Materials*, 2020, **13**, 4298.

2 I. Yu. Skvortsov, L. A. Varfolomeeva, M. S. Kuzin, A. F. Vashchenko, E. V. Chernikova, R. V. Tom and V. G. Kulichikhin, *Mendeleev Commun.*, 2022, **32**, 652.

3 J. H. Lee, J.-U. Jin, S. Park, D. Choi, N.-H. You, Y. Chung, B.-C. Ku and H. Yeo, *J. Ind. Eng. Chem.* 2018, **71**, 112.

4 S. P. Liu, K. Q. Han, L. Chen, Y. Zheng and M. H. Yu, *Appl. Mech. Mater.*, 2015, **723**, 652.

5 P. Rangarajan, J. Yang, V. Bhanu, D. Godshall, J. McGrath, G. Wilkes and D. Baird, *J. Appl. Polym. Sci.*, 2002, **85**, 69.

6 E. V. Chernikova, N. I. Osipova, A. V. Plutalova, R. V. Toms, A. Y. Gervald, N. I. Prokopov and V. G. Kulichikhin, *Polymers*, 2022, **14**, 5222.

7 W. Deng, A. Lobovsky, S. T. Iacono, T. Wu, N. Tomar, S. M. Budy, T. Long, W. P. Hoffman and D. W. Smith, Jr., *Polymer*, 2011, **52**, 622.

8 S. F. Mahmood, B. L. Batchelor, M. Jung, K. Park, W. E. Voit, B. M. Novak and D. Yang, *Carbon Lett.*, 2019, **29**, 605.

9 R. V. Toms, A. Yu. Gervald, N. I. Prokopov, N. I. Osipova, A. V. Plutalova and E. V. Chernikova, *Polym. Sci., Ser. B*, 2022, **64**, 294.

10 B. Fan, J. Wan, A. McKay, Z. Qu and S. H. Thang, *Polym. Chem*., 2020, **11**, 5649.

11 *RAFT Polymerization: Methods, Synthesis, and Application*, eds. G. Moad and E. Rizzardo, Wiley-VCH, Weinheim, 2022.

12 H. E. Kissinger, *Anal. Chem.*, 1957, **2**, 1702.

Received: 20th February 2023; Com. 23/7104