TEMPO-mediated radical polymerization in the synthesis of poly(methyl methacrylate) macromonomer

Mikhail Yu. Zaremski,* Elvin E. Aliev, Elizaveta S. Garina and Nikolay S. Melik-Nubarov

Department of Chemistry, M. V. Lomonosov Moscow State University, 119991 Moscow, Russian Federation.
E-mail: zaremski@mail.ru

A new synthesis of poly(methyl methacrylate) vinyl-terminated macromonomer is performed using the disproportionation between propagating methyl methacrylate radical and nitroxide TEMPO. The ability of the macromonomer to polymerize and copolymerize with styrene and poly(ethylene glycol) methacrylate was confirmed by GPC and isothermal calorimetry.
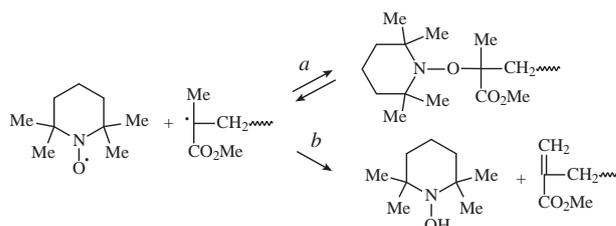
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The production of macromonomes is of significant interest since the terminal double bonds can further react to form graft, star-like, comb-like or brush copolymers. In comparison with linear macromolecular analogues, such copolymers have a more compact conformations of macromolecules in solutions, they are readily soluble in a variety of solvents, highly sensitive to external stimuli and have low intrinsic viscosity in solutions.[1] It is usually not necessary to search for high molar percentages of macromonomer in the copolymer, however, it is necessary for the terminal group of macromonomer being able to copolymerize with other monomers. Among various macromonomers (meth)-acrylate-based vinyl macromonomers are widely used for the synthesis of amphiphilic polymeric surfactants, reactive dispersants and soluble resins,[2,3] coatings and adhesives,[4] biologically active objects,[5] and others.[6]

Macromonomers of poly(methyl methacrylate) (PMMA) can be synthesized using specific techniques and reagents *via* anionic,[7,8] addition–fragmentation transfer,[9] or catalytic chain transfer[10] polymerization approaches or end group modification.[11] However, insufficient double bond yields are obtained when using chain transfer agents of (meth)acrylate monomers due to the interaction of the radical centre with the catalyst.[4] Also anionic polymerization is restricted due to stringent requirements on reaction conditions and monomer purity.

On the other hand, PMMA macromonomers are formed directly in the course of radical polymerization of methyl methacrylate (MMA) as a result of chain termination *via* either disproportionation or chain transfer to monomer. Due to steric limitations caused by the presence of α-methyl groups, chain termination occurs mainly not through the recombination path, but through disproportionation. As a result, no more than a half of macromolecules of thus formed PMMA contains terminal vinyl bond while the other molecules are completely saturated. Obviously, this approach is of no interest for practical application since it is not possible to separate molecules with a terminal double bond from the others.

Nitroxide-mediated radical polymerization of MMA is known to provide enhancing the fraction of vinyl-terminated macromolecules up to nearly 100%. This refers to nitroxide-mediated radical polymerization. Nitroxide-mediated polymerization of the vast majority of vinyl monomers proceeds *via* the formation of dormant species **1** capable of undergoing homolytic decomposition and reinitiating the further chain growth (Scheme 1, pathway *a*).[12] Under the same conditions, MMA polymerization is accompanied by disproportionation resulting in the formation of low molecular hydroxylamine and vinyl-terminated macromolecule **2** (pathway *b*). As far as the process loses the features of 'living' polymerization, this reaction is considered undesirable and much efforts are directed to avoid this disproportionation.[13,14] The present work was aimed at the employment of this 'undesirable' reaction to obtain a macromonomer, PMMA with a terminal double bond, and to demonstrate its ability to undergo polymerization and copolymerization processes.

It was previously shown[15] that a living adduct PMMA–TEMPO **1** (see Scheme 1) is formed with a probability of about 80% at each elementary step of TEMPO-mediated polymerization of MMA at 120 °C. At the same time, the probability of the formation of disproportionation products, *i.e.* hydroxylamine of TEMPO and vinyl-terminated polymer **2** is 20% for each act of TEMPO interaction with the growing chain. Therefore, after 10
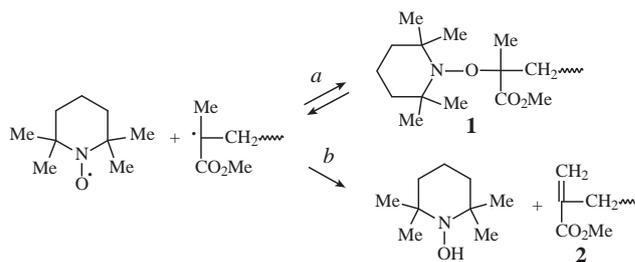
Scheme 1

acts of this interaction, about 90% of the polymer should contain terminal vinyl group and after 20 acts, about 99% of the macromolecules should be converted into a macromonomer.

The concentration of nitroxides during the polymerization usually decreases rapidly as the initiator decays, but then can increase, indicating a significant contribution from the process of the 'living' PMMA–TEMPO adducts decay.[16] As long as these 'living' adducts exist in the system, their decay will inevitably lead to the partial release of free nitroxide as by-product in the irreversible bimolecular termination of PMMA-radicals formed. After the entire polymer has transformed into a macromonomer, the release of TEMPO should stop. Thus, the retardency of TEMPO release during polymerization can serve as an 'indicator' of the completion of the process of disproportionation and formation of a macromonomer.

To follow disproportionation process, we analyzed the changes in TEMPO concentration during TEMPO-mediated polymerization varying (i) AIBN and TEMPO concentrations at a constant molar ratio (1:1) [Figure 1(a)], (ii) AIBN concentration at a constant TEMPO concentration (10 mM) [see Figure 1(b)], and (iii) monomer concentration at a constant MMA/AIBN/TEMPO ratio. In all studied systems, three clearly discernible regions were distinguished in the kinetic curves. A rapid decomposition of the initiator results in the formation of radicals which capture nitroxides thus explaining an initial sharp drop in the nitroxide concentration (see Figure 1). Further, an increase in the concentration of free TEMPO is observed, wich reflects the formation of free nitroxides caused by the irreversible termination of the growing chains elicited from the decay of the 'living' adducts. The third part of the curve corresponds to the exhaustion of the 'living' PMMA–TEMPO adducts and therefore TEMPO concentration reaches constant level.

As shown in Table 1, addition of 100 mM TEMPO and AIBN results in a complete inhibition of polymerization. A 10-fold decrease in both concentrations while maintaining equimolar ratio between them resulted in a 7% yield of the polymer with M_n about 13–25 kDa and M_w/M_n ~2.0–2.7. Neither yield of the polymer, nor the time required for the exhaustion of 'living' adducts and the curve to reach a plateau did not depend on absolute concentration if their ratio was about 1 [see Figure 1(a)].

A 1.5-fold increase in AIBN concentration at a constant 10 mM concentration of TEMPO resulted in a decrease in the
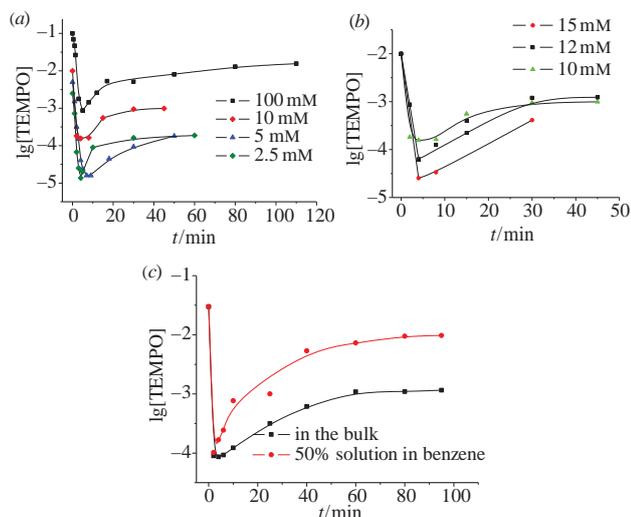
Table 1 Yield and molecular mass characteristics of the MMA macromonomer obtained under various conditions.

[TEMPO]/ mM	[AIBN]/ mM	[MMA] (%)	t/ min	Yield (%)	M_n/ kDa	$M_{n(theor.)}$/ kDa	M_w/M_n
100	100	100	120	0	-	-	-
10	10			7.0	13.8	6.6	2.0
5	5			7.6	16.2	14.3	2.7
2.5	2.5			7.1	25.4	26.7	2.1
10	12	100	100	18.3	13.1	17.1	2.3
10	15			23.7	9.5	22.3	2.6
30	36	100	150	10.2	4.09	3.2	1.35
30	36	50		<2			

concentration of free TEMPO [see Figure 1(b)]. This causes an increase in PMMA yield to 24%. At the same time, the M_n value diminishes to 9.5 kDa and the polydispersity coefficient rises from 2.0 to 2.6 (see Table 1).

When polymerization is carried out in a 50% solution of benzene, the yield of PMMA drops sharply below 2%. This is naturally associated with an increase in the stationary concentration of TEMPO by an order of magnitude compared with the bulk polymerization [see Figure 1(c)].

As far as disproportioning termination of the propagating chains and nitroxides is irreversible, molecular mass of PMMA differs from the theoretical one calculated for living chains (see Table 1):

$$M_n = \frac{[M]_0}{[T]_0} \, q \, m,$$

where $[M]_0$ and $[T]_0$ are initial concentrations of MMA and TEMPO, q is conversion and m is molecular mass of MMA.

Optimum conditions for the synthesis of PMMA macromonomer found from these experiments corresponded to [AIBN] = 36 mM and [TEMPO] = 30 mM, duration of the synthesis was 2 h.[†] Under these conditions, the yield of macromonomer is about 10%, its M_n = 4090, and polydispersity index M_w/M_n = 1.35.

The presence of terminal vinyl bond was confirmed by ^{1}H NMR. The spectrum contained signals from vinyl protons at 6.21–6.11 (d, 1H, =CH–*H*) and 5.57–5.48 ppm (d, 1H, =C*H*–H) (see Online Supplementary Materials). Their content relative to methyl protons for the ester group (3.61 s, 3H, MeO), methylene protons of the main chain (2.08–1.60 m, 2H, CH₂) and α-methyl protons of MMA (1.25–0.85 m, 3H, Me) corresponded to about 97% of the vinyl-terminated macromolecules. NMR data also confirmed that the terminal double bond is formed due to the removal of a hydrogen atom by nitroxyl from the α-methyl rather than from the methylene group of the growing radical.

The obtained PMMA can be homopolymerized or copolymerized with poly(ethylene glycol) methacrylate (PEGMA) in benzene (PEGMA with M_n = 1900 was obtained as described[17]). (Co)polymerization of the macromonomer was carried out in the 48 mM macromonomer solution in benzene in the presence of 0.1 M AIBN at 70 °C *in vacuo*.[‡] In the first case, a poly(PMMA) brush structure is formed with M_n = 14800, M_w/M_n = 1.76 (Figure 2). One can see that the MWD curve of the homopolymerization product does not contain shoulder of the initial macromonomer, indicating that the whole macromonomer has turned into a brush-like polymer. In the second case, an

Figure 1 Dependence of TEMPO concentration on the time of macromonomer synthesis; (*a*) by varying the concentration of TEMPO and AIBN with their constant ratio (1 : 1); (*b*) by varying the concentration of AIBN with the constant [TEMPO] = 10 mM; (*c*) upon polymerization in bulk and benzene, [AIBN] = 36 mM, [TEMPO] = 30 mM.
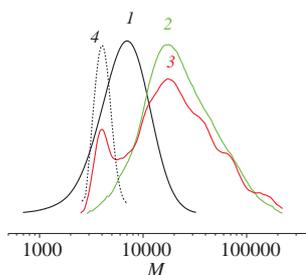
Figure 2 MWD curves for (*1*) the macromonomer, (*2*) the product of homopolymerization of macromonomer in benzene, [PMMA] = 48 mM (20%), (*3*) the product of its copolymerization with PEGMA in benzene, [PMMA] = 48 mM (20%), [PEGMA] = 100 mM (20%), and (*4*) PEGMA.

amphiphilic graft copolymer with a bimodal MWD containing an admixture of unreacted PEGMA was obtained (M_{peak} corresponding to the copolymer was about 17 kDa). The copolymer also does not contain the starting macromonomer. The second evidence for complete transformation of a macromonomer into a copolymer is that, unlike the macromonomer, the product does not precipitate into methanol.

The fact that the obtained polymers are macromonomers capable of polymerization is also confirmed by isothermal calorimetry data. This technique is very convenient for continuous recording of the polymerization rate w by heat flow dQ/dt, because the polymerization is an exothermic reaction with the standard molar enthalpy H of –10–20 kcal mol^{-1}. These values are connected by direct proportionality:

$$w\,\Delta H = dQ/dt.$$

Figure 3 shows the heat release curves during homopolymerization of the PMMA macromonomer and its copolymerization with styrene. The reaction is characterized by a heat release curve typical of radical polymerization, which drops exponentially according to the monomer consumption. Unfortunately, the calorimetric curves cannot be recalculated into kinetic polymerization curves because the magnitude of the heat of the macromonomer polymerization is unknown.

Products of (co)polymerization of the macromonomers with MMA are brush-like macromolecules, whose structure is schematically presented in Figure 4. These data show that the obtained PMMA is a macromonomer capable of homo- and copolymerizing to form brush-like polymers.
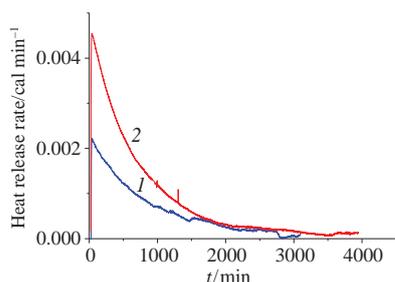

Figure 3 Kinetic curves of heat release during (*1*) homopolymerization of the PMMA macromonomer and (*2*) its copolymerization with styrene in benzene. [PMMA] = 48 mM (20%); [styrene] = 280 mM.

‡ (Co)polymerization of the macromonomer was carried out in the solution of the macromonomer (60 mg) and AIBN (4.92 mg) in benzene (0.3 ml), or in the solution of the macromonomer (60 mg), PEGMA (60 mg) and AIBN (4.92 mg) in benzene (0.3 ml), or in the solution of the macromonomer (60 mg), styrene (0.01 ml) and AIBN (4.92 mg) in benzene (0.3 ml). The polymers were isolated by lyophilization from benzene *in vacuo*.
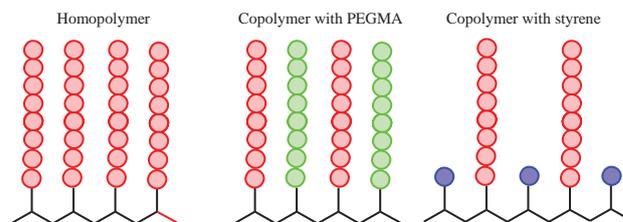

Figure 4 The schematic structure of obtained (co)polymers. Here the red symbols designate the side chains of PMMA with number-average degree of polymerization of 40, the green symbols designate the PEG chains with number-average degree of polymerization of 43, and the blue symbols designate the phenyl groups.

To conclude, we have accomplished simple and effective synthesis of PMMA-macromonomers using nitroxide-mediated radical polymerization. The results of this work are promising for macromolecular design of graft and brush copolymers.

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2020.09.025.

References

1 I. V. Ivanov, T. K. Meleshko, A. V. Kashina and A. V. Yakimansky, *Russ. Chem. Rev.*, 2019, **88**, 1248.
2 M. Bandiera, S. Hamzehlou, F. Ruipérez, M. Aguirre, R. Balk, M. J. Barandiaran and J. R. Leiza, *Polym. Chem.*, 2019, **10**, 1769.
3 M. Zhang and R. A. Hutchinson, *Macromolecules*, 2018, **51**, 6267.
4 N. Heidarzadeh and R. A. Hutchinson, *Polym. Chem.*, 2020, **11**, 2137.
5 S. V. Kurmaz, T. N. Rudneva and N. A. Sanina, *Mendeleev Commun.*, 2018, **28**, 73.
6 W. J. Stevens, *PhD Thesis*, Loughborough, 1996, https://hdl.handle.net/2134/10474.
7 P. Lutz, P. Masson, G. Beinert and P. F. Rempp, *Polym. Bull.*, 1984, **12**, 79.
8 K. Ishizu and T. Fukutomi, *J. Polym. Sci., Polym. Chem. Ed.*, 1989, **27**, 1259.
9 S. A. F. Bon, S. R. Morsley, C. Waterson and D. M. Haddleton, *Macromolecules*, 2000, **33**, 5819.
10 Y. Li and B. B. Wayland, *Macromol. Rapid Commun.*, 2003, **24**, 307.
11 C. Loubat, S. Soulier and B. Boutevin, *Polym. Bull.*, 2001, **45**, 487.
12 J. Nicolas, Y. Guillaneuf, C. Lefay, D. Bertin, D. Gigmes and B. Charleux, *Prog. Polym. Sci.*, 2013, **38**, 63.
13 E. Guégain, Y. Guillaneuf and J. Nicolas, *Macromol. Rapid Commun.*, 2015, **36**, 1227.
14 Yu. L. Kuznetsova, P. G. Mozaleva, A. S. Vavilova and E. A. Kalinina, *Russ. Chem. Bull, Int. Ed.*, 2020, **69**, 763 (*Izv. Akad. Nauk, Ser. Khim.*, 2020, 763).
15 M. Souaille and H. Fischer, *Macromolecules*, 2001, **34**, 2830.
16 M. Yu. Zaremski, A. B. Zhaksylykov, A. P. Orlova, E. S. Garina, G. A. Badun, M. B. Lachinov and V. B. Golubev, *Polym. Sci., Ser. A*, 2005, **47**, 526 (*Vysokomol. Soedin., Ser. A*, 2005, **47**, 886).
17 S. Zalipsky, C. Gilon and A. Zilkha, *J. Macromol. Sci., Part A: Chem.*, 1984, **21**, 839.