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A facile one pot strategy for the synthesis of well-defined polyacrylates from acrylic acid *via* RAFT polymerization†

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A facile one pot strategy for the preparation of linear and hyper-branched polyacrylates has been successfully developed by the combination of *in situ* esterification of acrylic acid with halogenated compounds promoted by 1,1,3,3-tetramethylguanidine (TMG) and RAFT polymerization.

In chemistry, the one pot strategy can enhance the efficiency of chemical reactions since all the reactants undergo successive reactions in just one reactor, and it is greatly desired by chemists due to its avoidance of arduous separation and purification processes with respect to the intermediate compounds. Therefore, it can save considerable time and resources. The one pot method has been intensively studied and widely used in organic synthesis.[1] Recently, much attention has been paid to the application of the one pot strategy in polymer chemistry[2] by the combination of polymerization with compatible reactions. For example, Sawamoto and coworkers synthesized gradient polymers in a one pot fashion *via* a combination of the *in situ* transesterification of acrylate with alcohols catalyzed by metal alkoxide and transition metal-catalyzed living radical polymerization.[3] Tao *et al.*[4] developed a one pot synthetic method for the synthesis of polymethacrylates by combination of lipase-catalysed transesterification of methacrylate and atom transfer radical polymerization (ATRP) or reversible addition fragmentation chain transfer (RAFT) radical polymerization. Similar work was also carried out by Martin Möller *via* the combination of enzymatic transacylation with light-controlled polymerization.[5] However, all of the approaches mentioned above are more suitable for the preparation of copolymers, rather than homopolymers, due to the reduced efficiency of the transesterification reaction between acrylates and alcohols.

Recently, our group found that 1,1,3,3-tetramethylguanidine (TMG) could be used to efficiently promote the esterification

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reaction of acrylic acid (AA) with halogenated compounds to give acrylates with almost 100% yields in a short time at room temperature. Encouraged by the high efficiency of the TMG-promoted esterification reaction and the excellent tolerance of RAFT polymerization[6] with respect to many monomers and solvents, we have developed a novel one pot strategy for the preparation of polyacrylates from acrylic acids by combination of the *in situ* esterification of acrylic acid with halogenated compounds and RAFT polymerization. Through this novel strategy, linear polyacrylates, including both homopolymers and copolymers, and hyperbranched polyacrylates with pendant functional groups can be directly synthesized from acrylic acids and halogenated compounds, thereby removing the preparation and purification procedures of acrylates.

Firstly, the esterification reaction of acrylic acid with ethyl iodide using TMG as a promoter was investigated by ¹H NMR spectroscopy in DMF at 70 °C. As shown in Fig. S1 (ESI†), the NMR results indicated that acrylic acid could be completely transformed into ethyl acrylate without any side-products. From the plots of yield *vs.* time (Fig. S2 in ESI†), it can be seen that the esterification reaction rate was very fast, with the yield as high as 90% after reaction for 10 min at 70 °C, and it could be completed in less than 30 min.

We then tried to synthesize linear polyacrylates in one pot by combining RAFT polymerization and the *in situ* TMG-promoted esterification of acrylic acid with halogenated compounds, as shown in Scheme 1. The process is very simple, with acrylic acid and TMG first being mixed in a reactor, followed by the addition of other reagents. After the reaction was performed in nitrogen atmosphere for 18 h at 70 °C, the resulting product was obtained as a sticky reddish matter, and was characterized by ¹H NMR spectroscopy in CDCl₃ (see Fig. 1a). These findings are consistent with those for polyethylacrylate (PEA) as reported in the literature.[7] The degree of esterification was calculated to be 100% by the intensity ratio of the methylene proton (4.05 ppm) in the ethyl group to the methine protons (2.23 ppm) in the polymer backbone, according to the ¹H NMR spectrum. These results demonstrate that PEA with a high degree of esterification
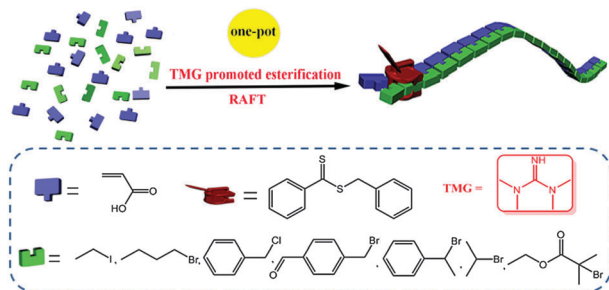
Scheme 1 Facile synthesis of polyacrylates *via* one pot RAFT polymerization with *in situ* TMG-promoted esterification of acrylic acid with halogenated compounds.
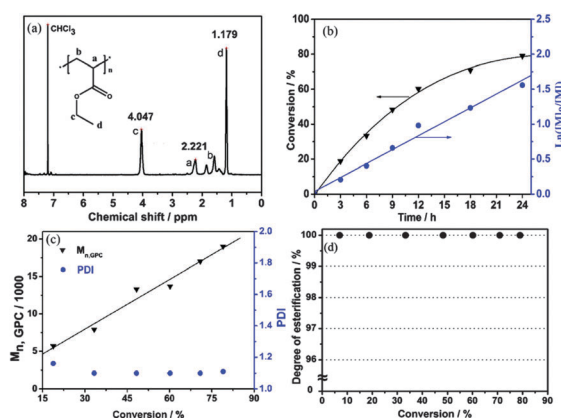

Fig. 1 One pot synthesis of polyacrylate by combining RAFT polymerization with *in situ* TMG-promoted esterification of AA with ethyl iodide: (a) ^{1}H NMR spectrum of the polymer obtained by the one pot strategy; (b) the monomer conversion and the kinetic curve *versus* polymerization time; (c) the molecular weight and the PDI of the polymer *versus* monomer conversion; (d) the degrees of esterification at different monomer conversions. Reaction conditions: [AA] = 50.0 mM; [TMG] = 50.0 mM; [ethyl iodide] = 50.0 mM; [benzyl dithiobenzoate] = 0.25 mM; [AIBN] = 0.025 mM in 10.0 mL DMF at 70 °C.

(a homopolymer) was obtained. Therefore, the one pot strategy was successfully achieved.

The kinetics of RAFT polymerization were studied, and the results are shown in Fig. 1. As shown in Fig. 1b, a linear relationship between $\ln([M]_0/[M])$ and the polymerization time demonstrates that the polymerization is a first-order reaction with respect to the monomer concentration and the number of

active radicals remains constant during the polymerization. Fig. 1c describes the molecular weight and molecular weight distribution as functions of the monomer conversion. The molecular weight of PEA increases linearly with monomer conversion and the molecular weight distribution remains narrow (less than 1.2) throughout the polymerization.

The one pot process involves two reactions. One is the *in situ* esterification reaction of acrylic acid with ethyl iodide promoted by TMG to generate ethyl acrylate. It was demonstrated that the esterification reaction of acrylic acid with ethyl iodide was very fast and was complete in less than 30 min using TMG as a promoter in DMF at 70 °C (Fig. S2 in ESI†). The second reaction is the polymerization of ethyl acrylate. In comparison with the esterification of acrylic acid, the polymerization of acrylate proceeds more slowly, as shown in Fig. 1b. In the early stage of the process, copolymerization of tetramethylguanidine acrylate and ethyl acrylate could have occurred, because tetramethylguanidine acrylate was not completely transformed into ethyl acrylate (Fig. S2 in ESI†). However, the copolymer of tetramethylguanidine acrylate and ethyl acrylate could be converted to the PEA homopolymer, as reported in our previous paper.[7] As shown in Fig. 1d, the degree of esterification can reach 100%, which indicates that the final product is a homopolymer of ethyl acrylate.

Furthermore, different mono-halogenated compounds were used *via* the one pot strategy to synthesize various polyacrylates, as shown in Table 1. For primary halogenated compounds, such as *n*-butyl bromide and benzyl chloride (entries 1 and 2 in Table 1), the corresponding polyacrylates can be obtained with a degree of esterification as high as 100%, calculated according to the ^{1}H NMR spectra in the ESI.† Moreover, the molecular weight distributions were narrow (the PDI is 1.11 and 1.18, respectively). The results show that this one pot strategy is very efficient for the preparation of different polyacrylates from acrylic acid, especially for acrylates that are not commercially available.

When secondary halogenated compounds were used, such as (1-bromoethyl)benzene and 2-bromopropane (entries 3 and 4 in Table 1), the esterification reactions also proceeded satisfactorily. The degree of esterification for both was measured to be 97% after reaction for 28 hours and 24 hours, respectively.

However, for tertiary halogenated compounds, such as ethyl 2-bromoisobutyrate (entry 5 in Table 1), the esterification reaction rate was slow and the degree of esterification was only 66% after the reaction was performed for 24 hours, which may be due to steric effects.

Table 1 One pot TMG-promoted esterification–RAFT polymerization of acrylic acid with halogenated compounds[a]

Entry	Halogenated compound	Time/h	Conv.[b]/%	Degree of esterification[c]/%	$M_{n,theo}$	$M_{n,GPC}$	PDI[d]
1	*n*-Butyl bromide	24	59	100	15 200	39 000	1.11
2	Benzyl chloride	24	86	100	28 000	47 700	1.18
3	(1-Bromoethyl)benzene	28	58	97	21 000	26 700	1.27
4	2-Bromopropane	24	73	97	17 000	26 200	1.78
5	Ethyl 2-bromoisobutyrate	24	91	66	28 000	51 700	1.15
6	4-(Bromomethyl)benzaldehyde	24	72	100	27 400	37 100	1.29

[a] [AA] = 12.5 mM; [TMG] = 12.5 mM; [halogenated compound] = 12.5 mM; [benzyl dithiobenzoate] = 0.0625 mM; [AIBN] = 0.00625 mM in 2.5 mL DMF at 70 °C. [b] Determined gravimetrically. [c] The proportion of carboxylates (degree of esterification) in the polymer was calculated by ^{1}H NMR. [d] Determined by GPC.
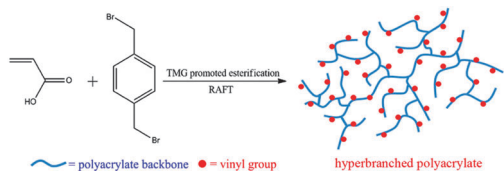
Scheme 2 Facile synthesis of hyperbranched polyacrylate *via* one pot RAFT polymerization with *in situ* TMG-promoted esterification.

This one pot strategy can be used not only in the preparation of the linear polyacrylates mentioned above, but also, in the preparation of hyperbranched polymers. Hyperbranched polymers with three-dimensional globular structures have attracted significant interest for a wide range of important applications,[8] such as coatings, adhesives, and drug carriers, due to their low viscosity, good solubility, high range of functionality, and much simpler and more cost-effective synthesis. Hyperbranched vinyl polymers have been mainly synthesized by self-condensing vinyl polymerisation (SCVP),[9] Strathclyde synthesis,[10] and the homopolymerization of asymmetric divinyl monomers,[11] which have been well reviewed in the literature.[12] However, the branching degree of the polymers obtained *via* the methods above was low. Recently, homopolymerization of symmetric divinyl monomers has been used to synthesize hyperbranched vinyl polymers *via* atom transfer radical polymerization (ATRP),[13] RAFT,[14] or chain walking,[15] which gives the obtained polymers a high degree of branching due to the potential branching unit of each monomer used in the polymerization. In addition, the unreacted pendant vinyl groups in the hyperbranched polymer can undergo further functionalization, post-polymerization, and cross-linking.

Hyperbranched polyacrylate can be prepared when a multi-halogenated compound is used to react with acrylic acid in the one pot strategy, as shown in Scheme 2. The process is similar to that for the synthesis of linear polyacrylate, except 1,4-bis(bromomethyl)benzene is used instead of a mono-halogenated compound. The reaction of acrylic acid with 1,4-bis(bromomethyl)benzene was demonstrated to be very efficient, with the yield reaching 100% in 5 min at 70 °C (Fig. S3 in ESI†). Therefore, the process can almost be considered as a

homopolymerization of divinyl monomers. The results in Table 2 (entries 3–7) indicate that both molecular weight and polydispersity increase dramatically with reaction time, due to the increased participation of multivinyl macromonomers at high monomer conversion, which suggests the formation of hyperbranched polyacrylate.[13] The formation of the hyperbranched polyacrylate was confirmed by the ^{1}H NMR spectrum, where the unreacted vinyl groups can be clearly observed in the polymer (peaks b and c from the vinyl functional group in Fig. S4 in the ESI†). In addition, the branch ratio can be accurately calculated by the eqn (S1) in the ESI.† As shown in Table 2, the hyperbranched polyacrylates obtained through this strategy have a high degree of branching, which was as high as 71% at the polymer yield of 65%. Furthermore, both the branch ratio and gel point[16] can be enhanced by decreasing the ratio of the monomer to the chain transfer agent, although the polymerization reaction will proceed more slowly.[6]

In conclusion, a novel and facile one pot strategy has been successfully developed for the preparation of polyacrylates from acrylic acid by the combination of RAFT polymerization and *in situ* esterification of acrylic acid with halogenated compounds promoted by TMG. Polymers with different structures are easily obtained by the appropriate choice of different halogenated compounds. The linear homopolyacrylates were obtained when primary and secondary mono-halogenated compounds were used, while the linear copolymers could be prepared when tertiary halogenated compounds were used. Moreover, hyperbranched polymers with a high branched ratio were obtained using di-halogenated compounds based on this one pot method. The results demonstrate that this one pot strategy is very facile and efficient, and can therefore be considered as a promising tool for the preparation of polyacrylates with different functionalities and architectures.

Table 2 Hyperbranched polymers synthesized *via* one pot RAFT polymerization and *in situ* TMG-promoted esterification of acrylic acid with 1,4-bis(bromomethyl)benzene[a]

Entry	AA/CTA	Time/h	Polymer yield[b]/%	Branch ratio[c]/%	$M_{n,GPC}$	PDI[d]
1	35/1	8.5	47	30	4000	1.81
2	35/1	10	53	Gelation		
3	10/1	3	16	23	990	2.37
4	10/1	6	29	42	1600	3.20
5	10/1	12	40	56	1800	4.69
6	10/1	24	50	59	3100	4.92
7	10/1	72	65	71	3600	5.83
8	5/1	58	49	65	2500	2.02

[a] [AA] = 10 mM; [TMG] = 10 mM; [1,4-bis(bromomethyl)benzene] = 5 mM; CTA = chain transfer agent = benzyl dithiobenzoate, [benzyl dithiobenzoate]/[AIBN] = 10/1; DMF 4.0 mL at 70 °C. [b] Determined gravimetrically. [c] Calculated from the ^{1}H NMR spectrum according to eqn (1) in the ESI. [d] Determined by GPC.

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