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ARTICLE TYPE

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

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

In chemistry, one pot strategy can enhance the efficiency of chemical reactions since all the reactants undergo successive reactions in just one reactor, and it is much desired by chemists due to its avoidance of arduous
15 separation and purification processes of the intermediate compounds. Therefore, it would save much time and resources. One pot method has been intensively studied and widely used in organic synthesis.[1] Recently, much attention has been paid on the one pot strategy in polymer chemistry [2] by combination of
20 polymerization with some compatible reactions. For example, Sawamoto and coworkers synthesized gradient polymers in 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]
25 developed a one pot synthetic method for synthesis of polymethacrylates by combination of lipase-catalytic transesterificaion of methacrylate and atom transfer radical polymerization (ATRP) or reversible addition fragmentation chain transfer (RAFT) radical polymerization. Similar work was
30 also done by Martin Möller via the combination of enzymatic transacylation with light-controlled polymerization.[5] However, the all approaches mentioned above are more suitable for preparation of copolymers, rather than homopolymers, due to the not high enough efficiency of transesterification reaction between
35 acrylates and alcohols.

Recently, our group found that 1, 1, 3, 3-tetramethylguanidine (TMG) could be used to efficiently promote the esterification reaction of acrylic acid (AA) with halogenated compounds to give acrylates with almost 100% yields in a short time at room
40 temperature. Encouraged by the high efficiency of the TMG promoted esterification reaction and the excellent tolerance of RAFT polymerization [6] to many monomers and solvents, we have developed a novel one pot strategy for preparation of polyacrylates from acrylic acids by combination of the in situ
45 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
50 compounds, getting rid of 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 ^{1}H NMR spectroscopy in DMF at 70℃. As shown in Fig. S1 (ESI), the
55 NMR results indicate that acrylic acid could be completely transformed into ethyl acrylate without any side-products. From the plots of yields vs. time (Fig. S2 in ESI), it can be seen that the esterification reaction rate was very fast, the yield was as high as 90% after reaction for 10 min at 70℃, and the reaction could be
60 completed in less than 30 minutes.

Then we 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, acrylic acid and
65 TMG were first mixed in a reactor, then other reagents were
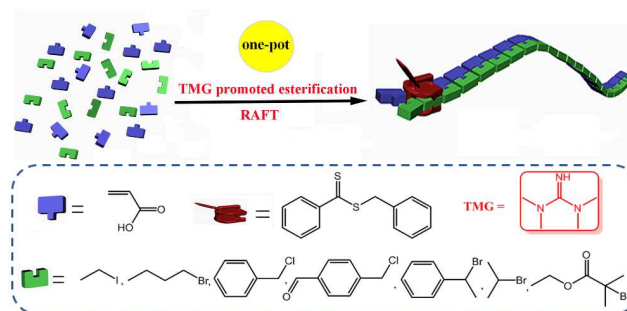
Scheme 1 Facile synthesis of polyacrylates via one pot RAFT with in situ TMG promoted esterification of acrylic acid with halogenated compounds.

added. After the reaction was performed in nitrogen atmosphere
70 for 18 h at 70℃, the resulting product was obtained as a sticky reddish matter, and characterized by ^{1}H NMR spectroscopy in CDCl$_3$ in Fig. 1a, which are consistent with those for PEA as reported in the literature. The degree of esterification was calculated to be 100% by the intensity ratio of the methylene
75 proton (4.05 ppm) in the ethyl group to the methine protons (2.23 ppm) in the polymer backbone according to the ^{1}H NMR spectrum. These results demonstrate that PEA with high degree of esterification (homopolymer) was obtained. Therefore, the one pot strategy was successfully achieved.

80 The kinetics of RAFT polymerization was studied, and the
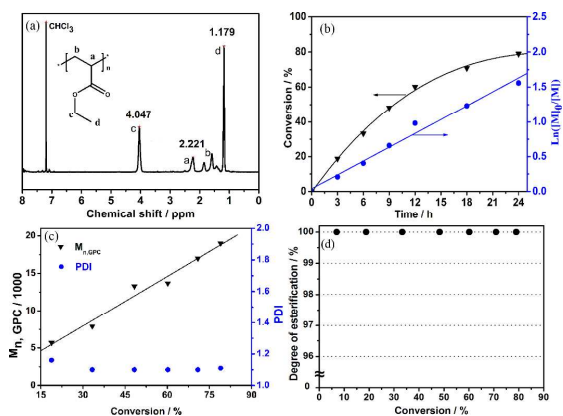
Fig. 1 One pot synthesis of polyacrylate by combining RAFT with in situ TMG promoted esterification of AA with ethyl iodide: (a) ^{1}H NMR spectrum of polymer obtained by one pot strategy; (b) monomer conversion and the kinetic curve versus polymerization time; (c) molecular weight and PDI of the polymer versus monomer conversion; (d) degrees of esterification at different monomer conversions. Reaction condition: [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□.

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 completed in less than 30 min using TMG as a promoter in DMF at 70℃(Fig. S2 in ESI). The other 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 might occur, 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 PEA homopolymer, as reported in our previous paper.[7] As shown in Fig. 1d, the degree of esterification can reach 100%, which indicates the final product is homopolymer of ethyl acrylate.

Furthermore, different mono-halogenated compounds were examined in 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 (entry 1 and 2 in Table 1), the corresponding polyacrylates can be obtained with the degrees of esterification as high as 100% calculated according to the ^{1}H NMR spectrums in ESI. Moreover, the molecular weight distributions were narrow (PDI are 1.11 and 1.18, respectively). The results show that this one pot strategy is very efficient for preparation of different polyacrylates from

acrylic acid, especially for the acrylates that are not commercially available.

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

entry	halogenated compounds	Time / h	Conv.[b] / %	Degree of esterification [c]/ %	$M_{n,theo}$	$M_{n,GPC}$	PDI[d]
1	n-butyl bromide	24	59	100	15200	39000	1.11
2	benzyl chloride	24	86	100	28000	47700	1.18
3	(1-bromoethyl)benzene	28	58	97	21000	26700	1.27
4	2-bromopropane	24	73	97	17000	26200	1.78
5	ethyl 2-bromoisobutyrate	24	91	66	28000	51700	1.15
6	4-(bromomethyl)benzaldehyde	24	72	100	27400	37100	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□. [b] Calculated by gravity. [c] The proportion of carboxylates (degree of esterification) in the polymer was calculated by ^{1}H NMR. [d] Determined by GPC.

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

However, for tertiary halogenated compound, 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 maybe due to its steric effect.

This one pot strategy can be used not only in the preparation of the linear polyacrylates as mentioned above, but also in the preparation of hyperbranched polymers. Hyperbranched polymers with three-dimensional globular structures have attracted significant interest in 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 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 diviny monomer,[11] which has been well reviewed in literatures.[12] However, the branching degree of the polymers obtained via the methods above was low. Resently, homopolymerization of symmetric divinyl monomer has been used to synthesize hyperbranched vinyl polymers via atom transfer radical polymerization (ATRP),[13] RAFT, [14] or chain walking,[15] which gives the polymers obtained with a high branching degree due to the potential branching unit of each monomer used in polymerization. And the unreacted pendant vinyl groups in hyperbranched polymer can undergo further functionalization, postpolymerization, and cross-linking.

Hyperbranched polyacrylate can be prepared when 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 using 1,4-bis(bromomethyl)benzene instead of mono-halogenated compound. The reaction of acrylic acid with 1,4-
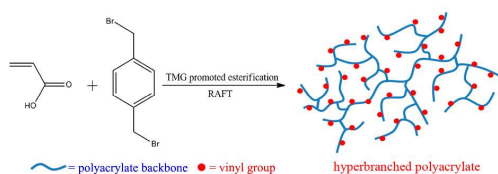
Scheme 2 Facile synthesis of hyperbranched polyacrylate via one pot RAFT with in situ TMG promoted esterification.

bis(bromomethyl)benzene was demonstrated to be very efficient, the yield can reach 100% in 5 min at 70□.(Fig. S3 in ESI) Therefore, the process can be considered almost as a homopolymerization of divinyl monomer. The results in Table 2 (entry 3-7) indicate that both molecular weight and polydispersity increase dramatically with reaction time, due to the increase 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 ^{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 ESI). And, the branch ratio can be accurately calculated by the equation 1 in ESI. As shown in Table 2, the hyperbranched polyacrylates obtained through this strategy have high branching degrees, 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 decrease the ratio of monomer to chain transfer agent, however, the polymerization reaction will proceed more slowly.[6]

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; [benzyl dithiobenzoate] /[AIBN] = 10/1; DMF 4.0 mL at 70□ . [b] Determined by gravity. [c] Calculated by ^{1}H NMR spectrum according the equation (1) in ESI. [d] Determined by GPC.

In conclusion, a novel and facile one pot strategy has been successfully developed for preparation of polyacrylates from acrylic acid by 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, the hyperbranched polymers with high branched ratio were obtained by using di-halogenated compounds based on this one pot method. The results demonstrate that this one pot strategy is very facile and efficient, therefore, it can be considered as a promising tool for preparation of polyacrylates with different functionalities and architectures.

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