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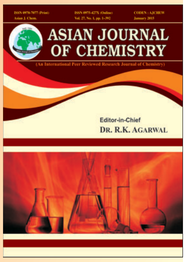

Preparation of Carboxyl-End-Group Poly(methyl methacrylate) and Polystyrene with Low Polydispersity by Atom Transfer Radical Polymerization Initiated with Chloroacetic Acid

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Carboxyl-end-group poly(methyl methacrylate) and polystyrene with low polydispersity were successfully prepared *via* atom transfer radical polymerization in bulk or in solution with chloroacetic acid as initiator and CuCl/N,N,N',N'-tetramethylethylenediamine as catalyst. The polymerizations showed the different polymerization rates depending on the feeding ratios for the atom transfer radical polymerization of both methyl methacrylate and styrene in either bulk or solution polymerization. The bulk polymerization for both monomers methyl methacrylate and styrene gave a faster polymerization rate and afforded a broader M_w/M_n of the obtained polymer. When the solvent was added into the polymerization system, the polymerization showed a moderate rate and yielded poly(methyl methacrylate) with the narrowest M_w/M_n of 1.17-1.21 and polystyrene with the narrowest M_w/M_n of 1.16-1.19, respectively. Polymerization kinetics showed that the polymerization proceeded by the normal atom transfer radical polymerization. The end groups of the well-defined poly(methyl methacrylate) and polystyrene were determined by ^{1}H NMR.

Keywords: Atom transfer radical polymerization, Carboxyl-end-group, Lower polydispersity, Poly(methyl methacrylate), Polystyrene.

INTRODUCTION

Several decades have witnessed the development of controlled/living radical polymerizations (CRP). Of three controlled/living radical polymerizations methods, atom transfer radical polymerization (ATRP) has turned out to be widely practiced, as it allows the controlled/living radical polymerizations of a wide variety of vinyl monomers with a diverse range of initiators and catalysts. Up to now, a large number of monomers have been successfully polymerized by ATRP, yielding polymers with determined chain length and low polydispersity[1-3].

To the best of our knowledge, a suitable initiator in ATRP process is vital for attaining a well-controlled radical polymerization system. Therefore, much attention has paid to finding effective initiators. Thus far, many kinds of organic compounds have been used as effective initiators such as haloalkanes[1,4-6], allyl halides[7], haloalkylbenzene[8-11], haloketones[12-14], haloesters[15-21], haloamides[22,23], halonitriles[24-26], sulfonyl chlorides[27-32], N-chlorosulfonamides[33], *etc*. Typically, Haddleton *et al.*[34] reported that they employed 2-bromo-2-methylpropionic acid as initiator for the ATRP of methyl methacrylate (MMA) and achieved effectively initiated polymerization except for the low initiation efficiency (0.3-0.4). Soon afterwards, Zhang and Matyjaszewski[35], on the other hand, revealed that α-halocarboxylic acids, such as 2-bromobutyric acid and 2-chloropropionic acid, were not effective for ATRP of styrene, with the low initiator efficiency of 0.03-0.2. Also, the polystyrenes obtained showed relatively broad polydispersities ranging from 1.25 to 1.75. However, carboxylic acid initiators with remote halogens, such as 4-(1-bromoethyl) benzoic acid and 4-[2-(2-bromopropionyloxy)ethoxy]benzoic acid, could afford polystyrene with lower polydispersity and an increased initiator efficiency of 0.7.

We have recently developed a novel initiating system with chloroacetic acid as effective initiator to initiate the stereospecific ATRP of acrylamide[36]. As one of the α-halocarboxylic acid, chloroacetic acid is easily available, low-cost and of relatively high activity of Cl-C bond (BDE 0.3059 a.u., Gaussian value). Also, chloroacetic acid holds two functional groups, the synthesized polymers would be equipped with functional end-groups of -COOH and -Cl, providing an easier access to further preparing the functionalized polymers. In this article, we detail our experimental results concerning the ATRP of methyl methacrylate and styrene with chloroacetic acid as functional initiator together with CuCl/N,N,N',N'-tetramethylethylenediamine (TMEDA) as the catalyst.

EXPERIMENTAL

Methyl methacrylate and styrene (chemically pure; Shanghai Chemical Reagent Co. Ltd., China) were vacuum-distilled after being dried by anhydrous magnesium sulfate before poly-merization. N,N,N',N'-tetramethylethylenediamine (TMEDA) (biochemical reagent, Shanghai Qianjing Chemical Reagent Plant, China), methanol (analytical reagent, Hangzhou Chemical Reagent Co. Ltd., China), chloroacetic acid (analytical reagent, Shanghai Linfeng Chemical Reagent Co. Ltd., China), dichloromethane (analytical reagent), toluene (analytical reagent) and anisole (99.7 %, analytical reagent, Shanghai Chemical Reagent Co. Ltd., China) were used as received. CuCl was synthesized from $CuCl_2$ (98 %, Shanghai Chemical Reagent Co. Ltd., China) and purified according to the literature[37].

Polymerizations

Bulk polymerization: A typical procedure was as follows: the chloroacetic acid, CuCl, TMEDA and monomer in appropriate ratios were added to a dry glass tube in turn. The tube was sealed under nitrogen after three freeze-vacuum cycles and then placed in an oil bath held at the desired temperature by a thermostat. The tube was taken out and cooled to stop the polymerization after the specified reaction time. The polymerization product was dissolved in CH_2Cl_2, precipitated in methanol and dried under a vacuum at 30 °C for 24 h. The conversion of the polymerization was determined gravimetrically.

Solution polymerization: The monomer methyl methacrylate and anisole, or monomer styrene and toluene were added to the glass tube with chloroacetic acid and CuCl/TMEDA, respectively. The tube was placed in an oil bath at a desired temperature for the specified time after three freeze-pump-thaw cycles. The polymerization was stopped by cooling the tube in ice water. The polymer was precipitated from methanol and dried under a vacuum.

Kinetic experiments: CuCl, TMEDA, monomer, solvent and chloroacetic acid in appropriate ratios were added to a tube. Sealed with a rubber septum, the tube was cycled three times between vacuum and nitrogen to remove oxygen and then placed in an oil bath kept at the desired temperature. After certain time intervals, samples were withdrawn from the reaction mixture using degassed syringes and processed with the procedures mentioned above.

Characterization: The conversion of the polymerization was determined gravimetrically. The ^{1}H NMR spectra were obtained with a 400 MHz INOVA instrument with $CDCl_3$ as a solvent. The chemical shifts were reported in parts per million with tetramethylsilane as an internal standard. The molecular weights and molecular weight distributions of the polymers were determined on a Waters 1515 gel permeation chromatograph (GPC) equipped with three columns (G1,000, 3,000HXL) and a differential refractometer detector. Polystyrene (PS) standards were used to calibrate the columns and tetrahydrofuran as the eluting solvent. It is worthwhile to notice that the measured molecular weight of PMMA *via* GPC could be different to its absolute molecular weight since the hydrodynamic volume of polystyrene and PMMA is different. Data were processed with Waters Millennium 32 software. All samples were run in THF at 25 °C.

RESULTS AND DISCUSSION

Table-1 presents the results of the ATRP of methyl methacrylate at 90 °C in bulk or in anisole and that of styrene at 110 °C in bulk or in toluene with different feeding ratios with chloroacetic acid as initiator and CuCl/N,N,N',N'-tetramethylethylenediamine (TMEDA) as the catalyst. The polymerizations showed the different polymerization rates depending on the feeding ratios for the ATRP of both methacrylate and styrene in either bulk polymerization or solution polymerization, that is, when the feeding ratio of [monomer]:[chloroacetic acid] increased, the polymerizations tended to get faster. A case in point was with the ATRP of methyl methacrylate in the bulk polymerization. When the feeding ratio of [chloroacetic acid]:[CuCl]: [TMEDA]:[monomer] was 1:1:2:100, the conversion of the monomer after 6 h of polymerization at 90 °C reached 63 %, which was distinctly higher than 45.7 % of conversion after the same polymerization time at the same temperature when the feeding ratio was 1:1:2:50. The similar occurrence was observed in the ATRP of methyl methacrylate in the solution polymerization and the ATRP of styrene in both bulk and solution polymerization. We supposed that this accelerated rate was plausibly due to the increased amount of radicals, which might be caused by the lack of control on polymerization. Furthermore the increase of initiator efficiency may also contribute a little to the increase of polymerization rate.

It was also worthwhile to notice that the bulk polymerization for both monomer methyl methacrylate and styrene gave a faster polymerization rate and afforded a broader M_w/M_n

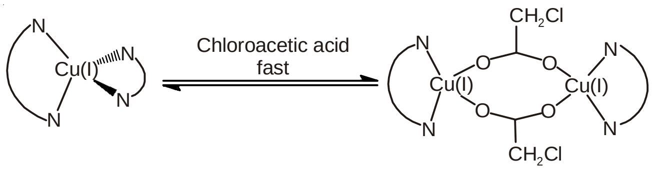
TABLE-1
RESULTS OF THE ATRP OF MMA AT 90 °C IN BULK OR IN ANISOLE AND THAT OF STYRENE AT 110 °C IN BULK OR IN TOLUENE WITH DIFFERENT FEEDING RATIOS

Run	Monomer	Feeding ratio[a]	Solvent[b]	Reaction time (h)	Conversion (%)	$M_{n,th}$[c]	M_n[d]	f[e]	M_w/M_n[d]
1	Methyl methacrylate	1:1:2:50	Bulk	6	45.7	2380	10270	0.23	1.43
2	Methyl methacrylate	1:1:2:100	Bulk	6	63.0	6390	21320	0.30	1.52
3	Methyl methacrylate	1:1:2:50	Anisole	16	23.8	1280	6230	0.21	1.21
4	Methyl methacrylate	1:1:2:100	Anisole	16	37.3	3850	10920	0.35	1.17
5	Styrene	1:1:2:50	Bulk	12	57.4	3080	12320	0.25	1.37
6	Styrene	1:1:2:100	Bulk	12	75.2	7950	26380	0.30	1.32
7	Styrene	1:1:2:50	Toluene	20	31.7	1750	9130	0.20	1.16
8	Styrene	1:1:2:100	Toluene	20	38.6	4100	11560	0.35	1.19

[a]Feeding ratio: [chloroacetic acid]:[CuCl]:[TMEDA]:[monomer]; [b]Solvent polymerization system: [monomer]/[solvent] = 1:1; [c]Theorectical molecular weights; [d]Determined by GPC; [e]Initiation efficiency.

of the obtained polymer than the solution polymerization, respectively. This meant that the bulk polymerization of the monomers was not well controlled under the conditions that were used. This might be because of the following two reasons: the fast initiation that could not be balanced by a relatively slow chlorine transfer reaction and the excess viscosity of the reaction mixture, which led to difficulty in controlling it. When the solvent was added into the polymerization system, the controllability became much better, although the polymerization rate decreased (Run 3,4 and 7,8). The system showed a moderate polymerization rate and yielded PMMA with the narrowest M_w/M_n of 1.17-1.21 and polystyrene with the narrowest M_w/M_n of 1.16-1.19, respectively.

However, we also noticed that there existed an enormous disparity between theorectical molecular weights $M_{n,th}$ and experimental molecular weights $M_{n,GPC}$ ($M_{n,th}$ = [(Conversion × $M_{Monomer}$ × $[Monomer]_0$)/$[Initiator]_0$] + $M_{Initiator}$, where $M_{Monomer}$ and $M_{Initiator}$ are the molecular weight of monomer and chloroacetic acid respectively). It is presumed that the unexpected molecular weights was subjected to lower initiation efficiency of the initiator (ranging from 0.20 to 0.35), which was possibly ascribed to the following causes. To start with, compared to secondary and tertiary α-halocarboxylic acid, primary α-halocarboxylic acid is more difficult to generate radicals, and also, the bond energy of C-Cl is higher than C-Br. Besides, in the ATRP system with the participation of chloroacetic acid, the acid would on one hand act as a functional initiator, and on the other hand, it could compete with the ligand for the coordination with copper(I), as was illustrated in the **Scheme-I**. This competition for the coordination could not only partially consume some proportion of the initiator but also interfere with the coordination of copper(I) and the amine ligand. Finally, the side reactions between monomers and chloroacetic acid should also be considered. All the above can cause the low initiator efficiency.



Scheme-I: Possible coordination of chloroacetic acid with the ATRP catalyst

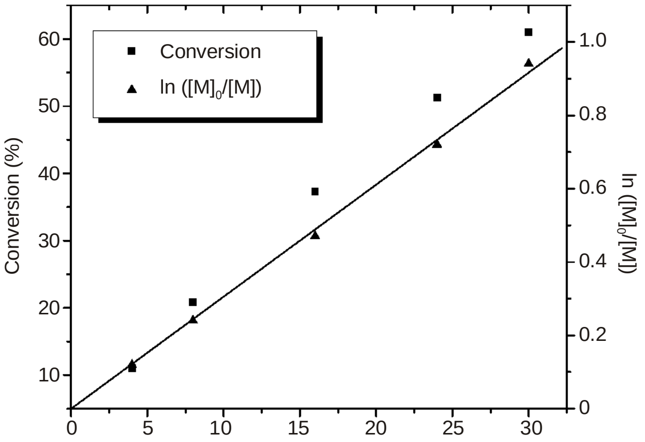


Fig. 1. Plots of conversion (%) and $\ln([M]_0/[M])$ *versus* the reaction time for the polymerization of methacrylate in anisole at 90 °C with a $[\text{chloroacetic acid}]_0:[CuCl]_0:[TMEDA]_0:[MMA]_0$ ratio of 1:1:2:100

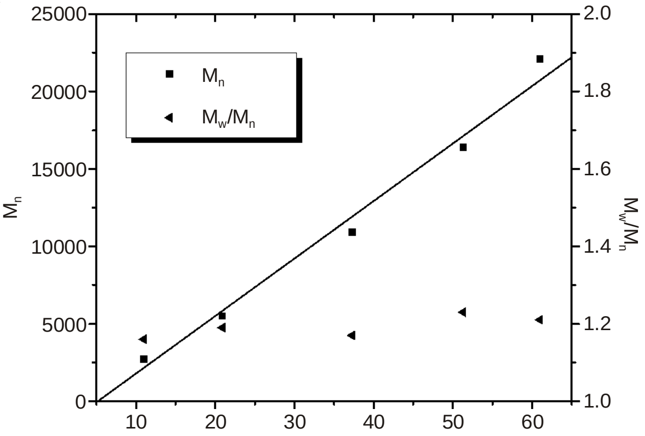


Fig. 2. Relationship between the number-average molecular weight (M_n) and polydispersity (M_w/M_n) with conversion (%) for the polymerization of methacrylate in anisole at 90 °C with a $[\text{chloroacetic acid}]_0:[CuCl]_0:[TMEDA]_0:[MMA]_0$ ratio of 1:1:2:100

To determine more about the initiation system, the polymerization kinetics of methyl methacrylate and styrene were carried out in anisole and toluene at a $[\text{chloroacetic acid}]_0:[CuCl]_0:[TMEDA]_0:[monomer]_0$ ratio of 1:1:2:100 at 90 and 110 °C, respectively. Figs. 1 and 2 depicted the kinetic and molecular weight and the polydispersity indexes data in the polymerization of methacrylate. The polymerization was first order with respect to the monomer. The number-average molecular weights (M_n) of the obtained PMMA was linearly increased with the increase of the conversion and the molecular weight distributions (M_w/M_n) of the polymers remained low throughout the polymerization (Fig. 2), ranging from 1.17 to 1.23. Similarly, Fig. 3 recounted that the monomer conversion in the polymerization of styrene proceeded in toluene at 110 °C increased with the time and also a linear relationship between the $\ln([M]_0/[M])$ and time was observed (Fig. 3). Also, the polydispersities of polystyrene remained around 1.19-1.25 as the conversion increased from 13.5 to 62.0 % (Fig. 4). These results indicated that the present polymerization proceeded by the normal ATRP and showed a living/controlled nature.

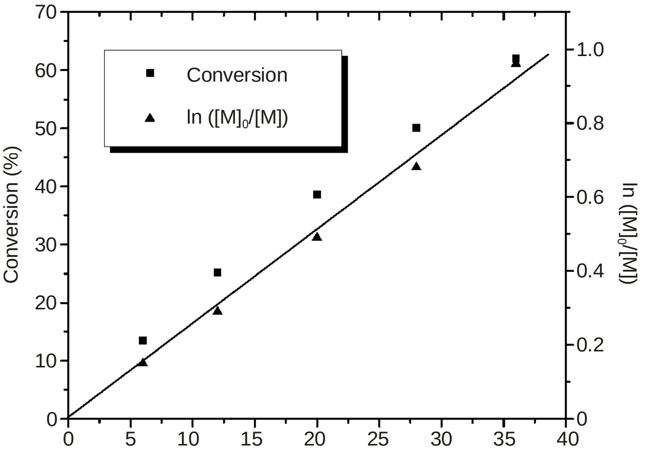


Fig. 3. Kinetics of the polymerization of styrene carried out in toluene at 110 °C with a $[\text{chloroacetic acid}]_0:[CuCl]_0:[TMEDA]_0:[styrene]_0$ ratio of 1:1:2:100

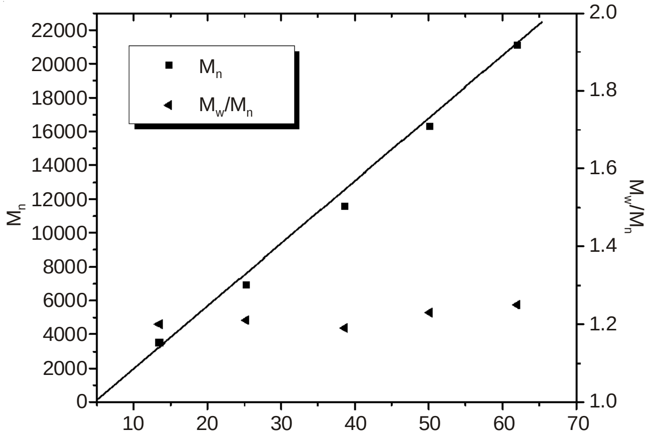


Fig. 4. Dependence of molecular weight and polydispersity on conversion for the polymerization of styrene carried out in toluene at 110 °C with a [chloroacetic acid]$_0$:[CuCl]$_0$:[TMEDA]$_0$:[styrene]$_0$ ratio of 1:1:2:100

The polymerization mechanism for monomer methyl methacrylate or styrene with chloroacetic acid/CuCl/TMEDA initiation system is supposed to proceed as depicted in **Scheme-II**. The initiation step includes the cleavage of chloroacetic acid into the radicals by the redox reaction of CuCl/ TMEDA with the initiator and the formation of a monomer radical *via* the reaction of the radical with the monomer. The monomer radicals react with the monomer to generate propagating chains. They may also directly accept the Cl from the oxidized $CuCl_2$/TMEDA to form the dormant species. The subsequent propagation is the same as in conventional ATRP.

The end groups of the well-defined PMMA and polystyrene were determined by ^{1}H NMR. The results are shown in Figs. 5 and 6, respectively.

In both spectra, the peak at 10.8 ppm is corresponding to the protons of -COOH on chloroacetic acid which was introduced to the end of the polymer chain during the polymerization. In addition, the peaks at 2.23 and 2.19 ppm in Fig. 5 are assigned to the protons of b (CH_2 from chloroacetic acid) and c for PMMA. Besides, the peak at 4.75 ppm in Fig. 6 is corresponding to the protons of c for polystyrene. These obviously indicate that the polymerization of methacrylate or styrene was initiated by radicals formed from the redox reaction of chloroacetic acid with CuCl/TMEDA.

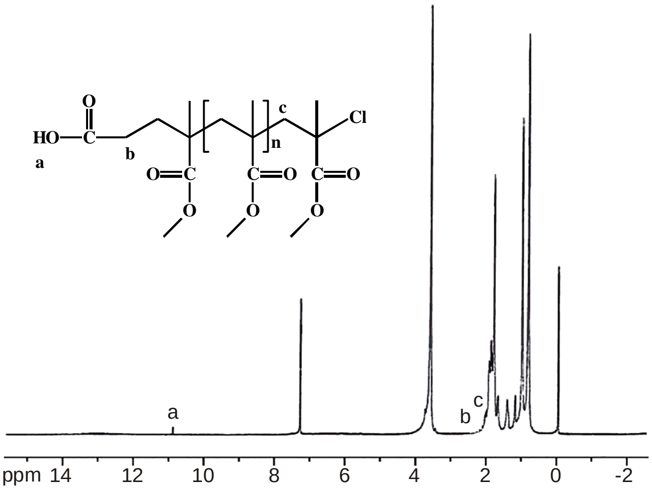


Fig. 5. ^{1}H NMR of PMMA prepared by ATRP with chloroacetic acid/CuCl/ TMEDA initiation system

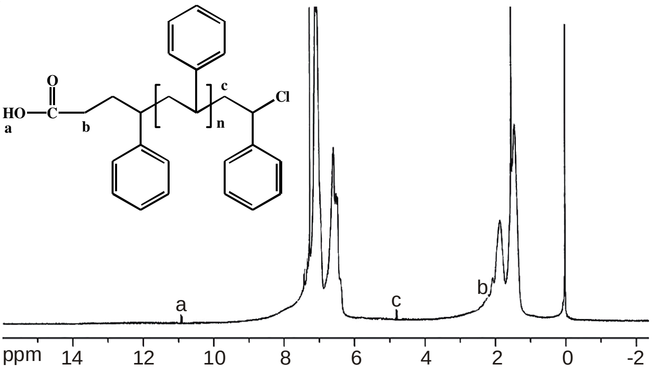
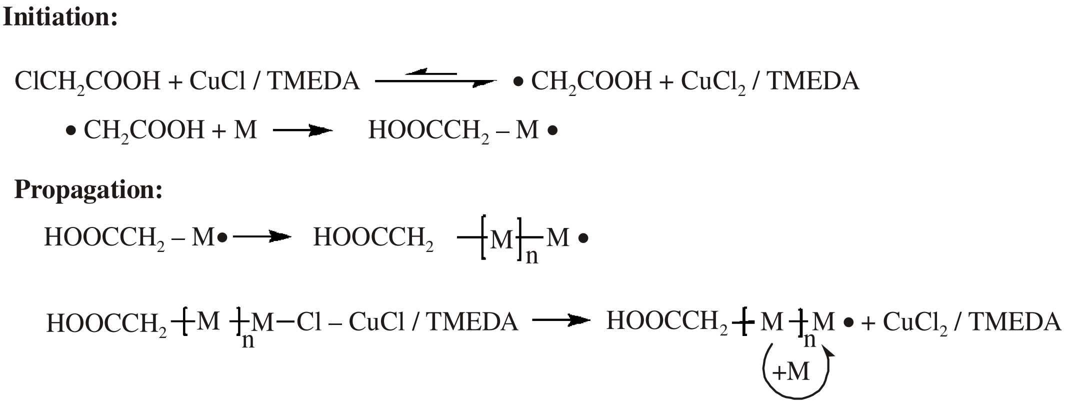


Fig. 6. ^{1}H NMR of polystyrene prepared by ATRP with chloroacetic acid/ CuCl/TMEDA initiation system

Conclusion

By using chloroacetic acid as a functional initiator and CuCl/N,N,N',N'-tetramethylethylenediamine (TMEDA) as the catalyst, we successfully obtained carboxyl-end PMMA and polystyrene with lower polydispersity. For both monomer methyl methacrylate and styrene, when the feeding ratio of [monomer]: [chloroacetic acid] increased, the polymerizations tended to get faster. The bulk polymerization gave a faster polymerization rate and afforded a broader M_w/M_n of the obtained polymer. The solution polymerization system manifested a moderate



Initiation:

$$ClCH_2COOH + CuCl / TMEDA \rightleftharpoons \bullet CH_2COOH + CuCl_2 / TMEDA$$

$$\bullet CH_2COOH + M \longrightarrow HOOCCH_2 - M \bullet$$

Propagation:

$$HOOCCH_2 - M\bullet \longrightarrow HOOCCH_2 \left[M \right]_n M \bullet$$

$$HOOCCH_2 \left[M \right]_n M - Cl - CuCl / TMEDA \longrightarrow HOOCCH_2 \left[M \right]_n M \bullet + CuCl_2 / TMEDA$$

Scheme-II: Polymerization mechanism with the chloroacetic acid/CuCl/TMEDA initiation system rate and yielded PMMA with the narrowest M_w/M_n of 1.17-1.21 and polystyrene with the narrowest M_w/M_n of 1.16-1.19, respectively. The synthesized PMMA and polystyrene was equipped with functional end-groups of -COOH and -Cl, providing an easier access to further preparing the functionalized polymers.

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