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Monomer Sequence Regulation in Main and Side Chains of Vinyl Copolymers: Synthesis of Vinyl Oligomonomers via Sequential Atom Transfer Radical Addition and Their Alternating Radical Copolymerization

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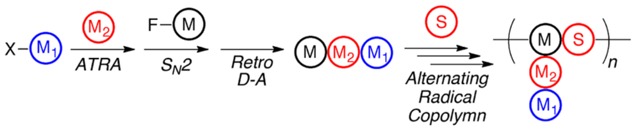
S *Supporting Information*



ABSTRACT: We propose a novel strategy of monomer sequence regulation in main and side chains of vinyl copolymers using sequential atom transfer radical addition (ATRA) for maleimide-ended sequence-regulated vinyl "oligomonomers" and their alternating radical copolymerization with styrene. To establish this strategy, a series of sequence-regulated vinyl oligomers were prepared by the ATRA of styrene (S) or methyl acrylate (A) to a halide-possessing A or S unit (methyl α-bromopropionate or 1-phenylethylhalide). The obtained halide-ended sequence-regulated vinyl oligomers were converted into maleimide-ended oligomonomers by S_N2 reaction with the potassium salt of furan-protected maleimide (M) followed by deprotection. The maleimide-ended oligomonomers were then radically copolymerized with styrene in an alternating fashion to result in sequence-regulated vinyl copolymers consisting of a controlled monomer sequence (SA, AS, AA, and SS) in the side chain and an alternating sequence (MS) in the main chain. The solubility of the copolymers depended on not only the monomer composition but also the sequence of the side chains, whereas the thermal properties were negligibly affected by the side-chain monomer sequences.

Monomer sequence regulation in synthetic polymers is still one of the most challenging topics in polymer science[1−4] because it may have great effects on their structures, properties, and functions, as observed in natural macromolecules such as proteins and nucleic acids that have fully controlled and programmed "monomer" sequences. In particular, the control of monomer sequence in vinyl copolymers is extremely difficult because they are usually produced via the chain copolymerization of multicomponent vinyl monomers, which proceeds statistically in most cases according to monomer reactivity ratios, mainly fitted by a chain-end model between the last monomer unit at the propagating species and the incoming monomers.[5,6] Although for some pairs of monomers, such as styrene and maleic anhydride or maleimide derivatives, alternating radical copolymerization exclusively proceeds to enable a form of monomer sequence regulation in an alternating fashion, a higher-ordered monomer sequence control is generally difficult to achieve.

Recently, along with significant progress in living polymerizations via various mechanisms,[7] there have been many studies on monomer sequence regulation based on several approaches.[8−26] We previously proposed a synthetic strategy for sequence-regulated vinyl copolymers based on heterotelechelic sequence-regulated vinyl oligomers[18] via sequential metal-catalyzed atom transfer radical additions (ATRAs)[27,28] followed by metal-catalyzed step-growth radical polymerization (Scheme S1 in the Supporting Information).[29,30] In this approach, vinyl monomers such as acrylate and styrene derivatives are added one by one to the carbon−chlorine bond originating from α-chloroesters via ATRA to be converted into oligomers consisting of the sequence-regulated vinyl monomer units, which are further converted into telechelic oligomers possessing a nonconjugated vinyl group and an active carbon−chlorine bond at each chain end. The obtained telechelic oligomers undergo step-growth radical polymerization, resulting in an equivalent structure to a vinyl chloride unit to form the targeted sequence-regulated vinyl copolymers consisting of styrene and acrylate units linked by vinyl chloride units. However, the molecular weights of the resulting polymers were relatively low ($M_n \sim 2 \times 10^3$) due to the step-growth mechanism, and it is difficult to know how the monomer sequence affects the properties of the sequence-regulated vinyl copolymers.

In this study, we propose a further developed strategy to regulate monomer sequences in the main and side chains of vinyl copolymers using sequential ATRA for the synthesis of sequence-regulated vinyl "oligomonomers" that possess a maleimide group at the chain end and their alternating radical copolymerization with styrene (Scheme 1). The monomer

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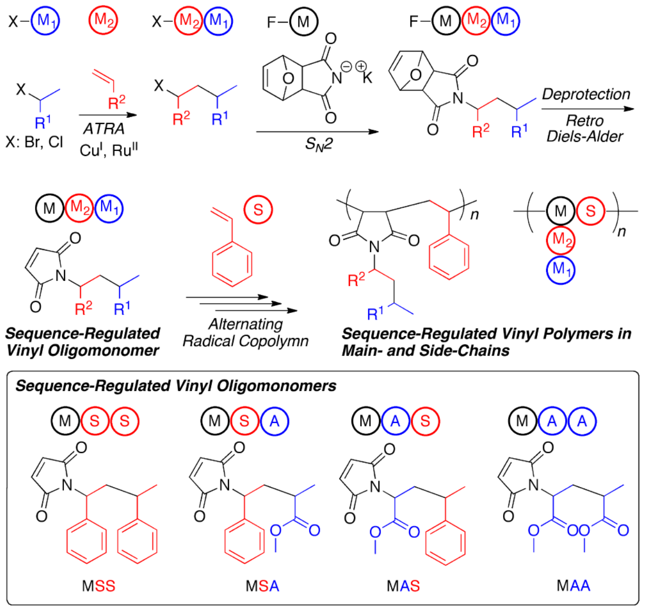
Scheme 1. Strategy for Monomer Sequence Regulation in Side and Main Chains of Vinyl Copolymers: Atom Transfer Radical Addition and Alternating Radical Copolymerization of Maleimide-Ended Sequence-Regulated Oligomonomers and Styrene



sequences are thus expected to be regulated both in the side chain by the sequential ATRA and in the main chain by the alternating radical copolymerization of the maleimide-ended oligomonomer and styrene. Although we have already reported monomer sequence regulation in the side chains of vinyl copolymers using olefin-ended sequence-regulated oligomonomers prepared via ATRA and their copolymerization with methyl acrylate, the incorporation of the oligomonomers into the main chain was not regulated, and their prevalence was as low as 40 mol % due to the low reactivity of the nonconjugated olefin group in the radical copolymerization.[31] The use of the maleimide group at the end of the sequence-regulated oligomonomers will enable not only the alternating sequences[32] in the main chain but also high molecular weights due to the high reactivity with styrene in the chain-growth radical copolymerization.

As the first study on this strategy, we herein synthesized a series of maleimide-ended oligomonomers consisting of dimeric units of styrene (S) and/or methyl acrylate (A) via ATRA followed by the introduction of a maleimide (M) group at the chain end and copolymerized them with styrene via free radical copolymerization. An appropriate reversible addition−fragmentation chain-transfer (RAFT) agent[33] was also employed for the alternating radical copolymerization to control the molecular weights of the vinyl copolymers as well as to analyze the monomer sequences in the main chain. The effects of the monomer sequence on the thermal properties and solubility of the copolymers were also investigated.

To synthesize the maleimide-ended styrene-methyl acrylate oligomonomer (MSA), ATRA was first conducted between styrene and excess methyl α-bromopropionate in the presence of CuBr and PMDETA at 60 °C to result in an almost exact 1:1 adduct (conversion of styrene: 81%). This adduct can be regarded as a heterodimer of styrene and methyl acrylate with a C−Br terminal (Br-SA). The isolated dimer with a C−Br bond undergoes an S_N2 reaction with furan-masked potassium maleimide followed by a retro Diels−Alder reaction for the deprotection of the furan mask to be converted into the corresponding maleimide-ended sequence-regulated vinyl oligomonomer consisting of styrene-methyl acrylate dimeric units (MSA).

The obtained products in each step were characterized by ^{1}H NMR spectroscopy. Upon the addition of styrene to methyl α-bromopropionate, the new characteristic methine proton (*e*) adjacent to the bromine atom appeared at approximately 5 ppm along with the phenyl (*f*) and methylene (*d*) protons of the styrene unit, indicating the formation of Br-SA (Figure 1B).

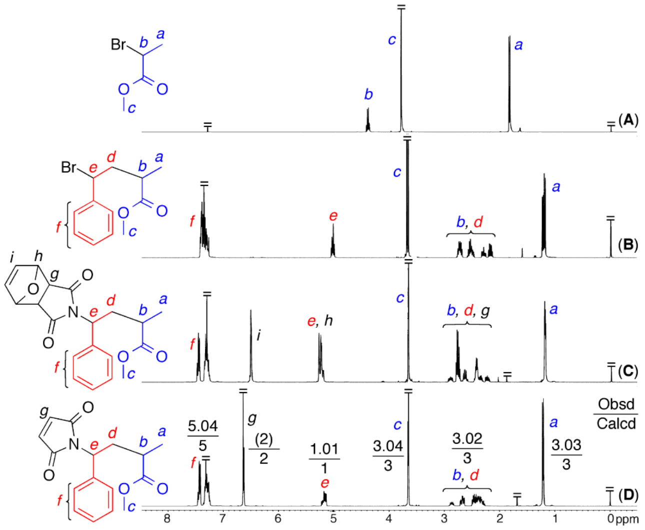


Figure 1. ^{1}H NMR spectra ($CDCl_3$, r.t.) of the products at each step for the synthesis of MSA.

After the S_N2 reaction, the methine proton (*e*) shifted slightly to a lower field along with the appearance of a furan-masked maleimide unit (*g*, *h*, and *i*) (Figure 1C). The furan group was then completely deprotected, as indicated by the disappearance of their peaks (Figure 1D). The peak intensity ratios of the purified products showed the successful formation of the maleimide-ended sequence-regulated oligomonomers with an ordered arrangement of styrene and methyl acrylate units (MSA), although they are mixtures of diastereomers and enantiomers (Figure 1D).

Furthermore, a complete set of the maleimide-ended sequence-regulated oligomonomers with dimeric units of styrene and/or methyl acrylate, i.e., MAS, MSS, and MAA, were successfully synthesized via similar pathways (Figure S1, Supporting Information).

The obtained maleimide-ended oligomonomers were then copolymerized with styrene at a 1:1 feed ratio using 1-phenylethyldithiobenzoate (PEDB) as a RAFT agent in the presence of AIBN in toluene at 60 °C. As shown in Figure 2A, both the oligomonomer (MSA) and styrene were consumed at the same rate almost quantitatively, suggesting that the alternating copolymerization proceeded irrespective of the side oligomer chain in the maleimide derivative.

The size-exclusion chromatography (SEC) curves of the obtained copolymers were narrow (M_w/M_n = 1.2−1.4) throughout the reactions and shifted to high molecular weights as the copolymerization proceeded (Figure S2, Supporting Information). The number-average molecular weights (M_n) of

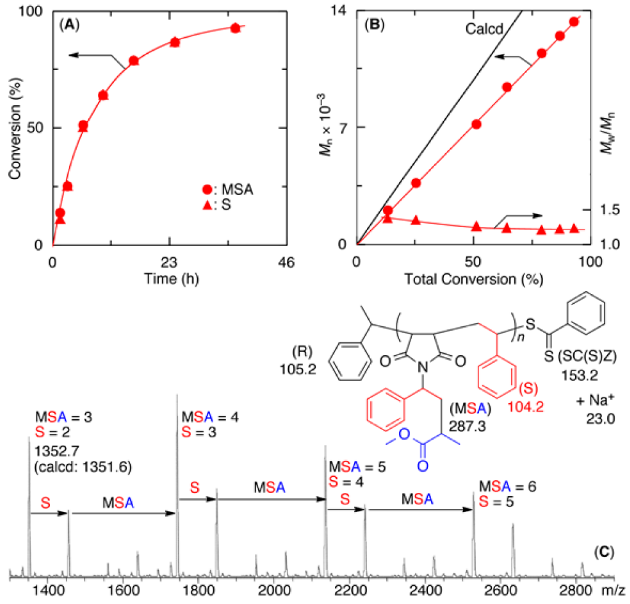


Figure 2. (A) Time−conversion curve for alternating RAFT copolymerization of MSA and styrene with AIBN in the presence of PEDB as a RAFT agent in toluene at 60 °C, (B) M_n and M_w/M_n curves, and (C) MALDI-TOF-MS spectrum of the obtained poly(MSA-*alt*-S) ($[MSA]_0$ = $[S]_0$ = 1.0 M, $[AIBN]_0$ = 5.0 mM, $[PEDB]_0$ = 20 mM).

the copolymers increased in direct proportion to the total monomer conversion, whereas they were smaller than the values calculated assuming that one molecule of the RAFT agent generates one copolymer chain (Figure 2B). However, the M_n measured by a multiangle laser light-scattering (MALLS) detector [M_n(MALLS) = 9600 at conversion of MSA/styrene = 52%/51%] was higher than that determined by SEC [M_n(SEC) = 7200] based on standard polystyrene calibration and was close to the calculated value [M_n(calcd) = 10300], suggesting that the low molecular weight by SEC is due to the compact hydrodynamic volume of the copolymers with side chains in comparison to that of polystyrene. Thus, the radical copolymerization of maleimide-ended oligomonomers and styrene can be controlled to result in copolymers with not only controlled molecular weights but also possibly controlled terminal groups using a suitable RAFT agent under appropriate conditions.

The copolymers obtained with PEDB as a RAFT agent were then analyzed by matrix-assisted laser desorption-ionization time-of-flight mass spectroscopy (MALDI-TOF-MS) to reveal the terminal groups as well as the monomer sequences in the copolymers. The spectrum is rather simple for multicomponent copolymers and basically consists of two series of peaks. The interval of the peaks in both series is ca. 391 Da, which corresponds to the sum of the masses of the MSA (287 Da) and styrene (104 Da) units. The peaks of the minor series can be assigned to the copolymers that have the same number ($m = l$) of MSA (m) and styrene (l) units in the chains and the RAFT agent unit at the terminals, whereas those of the major series can be assigned to the polymers with an extra maleimide unit ($m - l = 1$). In both series, the RAFT terminals are retained as indicated by the almost agreement of the observed masses with the calculated ones. These results indicate that the radical copolymerization of the oligomonomer (MSA) and styrene proceeds almost alternatingly to result in sequence-regulated vinyl copolymers possessing an alternating sequence (MS) in the main chain and a controlled sequence (SA) in the side chains.

The free radical copolymerization of a series of maleimide-ended sequence-regulated oligomonomers, i.e., MSS, MSA, MAS, and MAA, and styrene was also conducted at a 1:1 monomer feed ratio using AIBN in the absence of any RAFT agents in toluene at 60 °C. In all cases, both the oligomonomers and styrene were consumed at the same rate (Figure S3, Supporting Information) to give relatively high-molecular-weight polymers (M_n = 1−2 × 10^5) (Table 1). The incorporated ratios of oligomonomers and styrene, which were measured by the peak intensity ratios in the ^{1}H NMR spectra (Figure S4, Supporting Information), were almost 50/50, irrespective of the side chain sequences in the oligomonomers. Thus, all the chain radical copolymerizations proceeded in an alternating fashion to result in a series of sequence-regulated multicomponent vinyl copolymers with relatively high molecular weights.

The thermal properties of a series of copolymers were then evaluated by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). All the copolymers show glass transition temperatures (T_g) between 125 and 150 °C, depending on the vinyl monomer units in the side chains. It increases as the styrene content increases (Figure 3), which can be explained by the higher T_g of polystyrene than poly(methyl acrylate) (100 °C vs 10 °C). It is also noted that the T_g values are the same (T_g = 139 °C) for isomeric copolymers that have the same composition but opposite sequences in the side chains [poly(MSA-*alt*-S) and poly(MAS-*alt*-S)]. Thus, the T_g value is negligibly influenced by the monomer sequence in the dimeric units in the side chains of the sequence-regulated vinyl copolymers. The degradation temperatures (T_{d5}; temperature at 5% weight loss) of all the copolymers are over 360 °C due to the alternating main-chain sequences of the styrene and maleimide units. A slight difference in T_{d5} was observed, with the polymer with a higher styrene content and no ester groups

Table 1. Radical Copolymerization of Maleimide-Ended Oligomonomer (M_1) and Styrene (S)[a]

		conv. (%)[b]			incorp. (%)[b]	T_g[d]	T_{d5}[e]	cloud point (°C)[f]	cloud point (°C)[f]
M_1	time (h)	M_1/S	M_n[c]	M_w/M_n[c]	M_1/S	(°C)	(°C)	THF/MCH (45/55)	THF/MeOH (50/50)
MSS	7	97/98	135900	3.96	50/50	147	384	soluble	insoluble
MSA	5	>99/>99	166500	3.01	50/50	139	366	24.5	35.1
MAS	5	>99/>99	167500	2.66	49/51	139	361	20.2	12.9
MAA	8	98/98	138800	3.27	50/50	128	362	insoluble	3.0

[a]Polymerization condition: $[M_1]_0$ = $[S]_0$ = 1.0 M, $[AIBN]_0$ = 20 mM, toluene, 60 °C. [b]Determined by ^{1}H NMR. [c]Determined by SEC. [d]Obtained by differential scanning calorimetry. [e]Obtained by thermogravimetric analysis. [f]Determined by transmittance measurement: 10 mg/mL solution; cooling rate = 1 °C/min; wavelength = 500 nm.

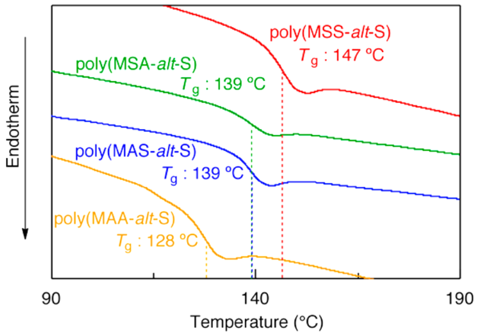


Figure 3. DSC curves and T_g values of a series of sequence-regulated vinyl copolymers in the main and side chains [poly(M_1-*alt*-S)] obtained in alternating free radical copolymerization of maleimide-ended oligomonomers (M_1: MSS, MSA, MAS, and MAA) and styrene with AIBN in toluene at 60 °C.

in the side chains [poly(MSS-*alt*-S)] having a slightly higher value (384 °C) than the other three (~360 °C) (Figure S5, Supporting Information). These results indicate that the side-chain monomer sequences have little effect on the thermal properties of the sequence-regulated vinyl copolymers consisting of alternating styrene-maleimide main-chain sequences and sequence-regulated styrene and/or methyl acrylate dimeric units in the side chain.

To see the effects on the solubility of the copolymers, the light transmittance of the polymer solutions at 500 nm was analyzed in two solvent mixtures with different polarity, such as THF/methylcyclohexane (MCH) (45/55) and THF/MeOH (50/50), at varying temperatures (Figure 4).

In THF/MCH (45/55), with a lower polarity, the copolymer with less polar dimeric styrene side chains was soluble at any temperature, while that with more polar dimeric methyl acrylate side chains was insoluble. The copolymers with the same composition but opposite monomer sequences in the side chains, i.e., poly(MSA-*alt*-S) and poly(MAS-*alt*-S), showed different solubilities; the copolymer with an outer styrene unit in the side chain [poly(MAS-*alt*-S)] was more soluble than poly(MSA-*alt*-S). An opposite solubility dependence was observed in a more polar solvent mixture, THF/MeOH (50/50). The copolymer with the more polar dimeric methyl acrylate was soluble even at 5 °C, whereas the copolymer with less polar dimeric styrene sequences was insoluble at any temperature. As for the copolymers with hetero dimeric sequences in the side chain, the copolymer with an outer methyl acrylate unit [poly(MSA-*alt*-S)] was more soluble in THF/MeOH (50/50) than that with an outer styrene unit [poly(MAS-*alt*-S)]. These results indicate that even one monomer in the side chains can affect the solubility of the copolymers and that the outer units are more important for determining the solubility.

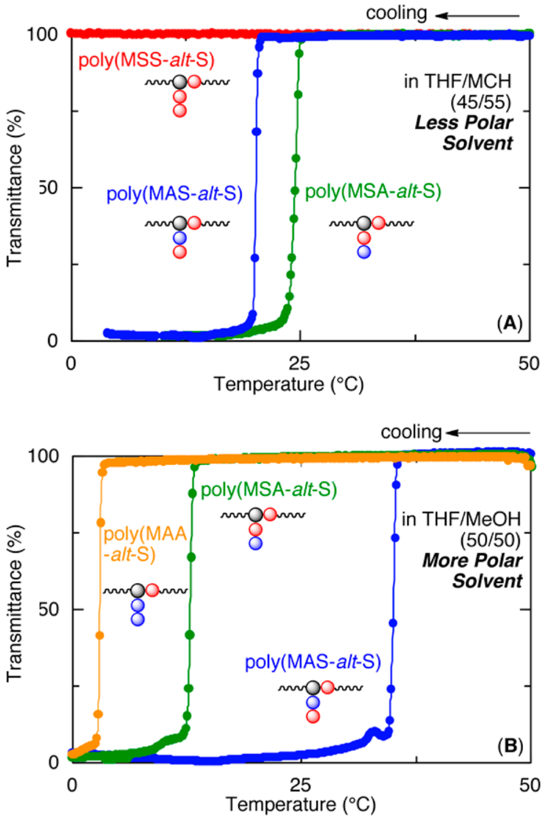


Figure 4. Transmittance of a series of sequence-regulated vinyl copolymers in the main and side chains [poly(M_1-*alt*-S)] obtained in alternating free radical copolymerization of maleimide-ended oligomonomers (M_1: MSS, MSA, MAS, and MAA) and styrene at varying temperatures in (A) THF/methylcyclohexane (45/55) and (B) THF/MeOH (50/50): 10 mg/mL; cooling rate = 1 °C/min; wavelength = 500 nm.

Furthermore, to elucidate the effects of precise sequence control on the polymer properties, two "sequence-unregulated" terpolymers, which possess random distribution of oligomonomer counterparts in the alternating maleimide-styrene copolymers, were prepared by radical terpolymerization of styrene/MSA/MAS (1/0.5/0.5) or styrene/MSS/MAA (1/0.5/0.5). In addition to the same consumption rate of the two oligomonomers (MSA vs MAS or MSS vs MAA), the total consumption rate of the oligomonomers (MSA+MAS or MSS+MAA) was the same as that for styrene (Figure S6, Supporting Information). This indicates the formation of the target sequence-unregulated terpolymers, i.e., poly((MSA/MAS)-*alt*-S) and poly((MSS/MAA)-*alt*-S) (Figure S7, Supporting Information). The thermal properties of the terpolymers were almost the same as those of the sequence-regulated copolymers with the same vinyl monomer compositions (Figures S8 and S9, Supporting Information). Interestingly, the solubilities of the sequence-unregulated terpolymers were between those of the corresponding sequence-regulated copolymers, respectively (Figure S10, Supporting Information). As the typical case, the cloud point (T_c) of poly((MSA/MAS)-*alt*-S) in THF/MeOH (50/50) was 24.8 °C, which was between 35.1 °C for poly(MAS-*alt*-S) and 12.9 °C for poly(MSA-*alt*-S). In addition, poly((MSS/MAA)-*alt*-S) showed less sensitive solubility change in THF/MCH (45/55). Thus, the precise sequence control affects the solubility, whereas there are almost no effects on the thermal properties.

In conclusion, we developed a novel strategy for controlling the monomer sequences in the main and side chains of vinyl copolymers using ATRA followed by S_N2 reactions for maleimide-ended sequence-regulated vinyl oligomonomers and their alternating radical copolymerization with styrene. This strategy enables the synthesis of sequence-regulated vinyl copolymers possessing controlled monomer sequences in both the main and side chains and relatively high molecular weights. The monomer sequence and composition in the side chains affected the solubility of the copolymers, although the thermal properties were negligibly influenced by the monomer sequence. This method can be applied to further monomer sequence regulation in both side and main chains using ATRA sequentially for other vinyl monomers as well as 1:2-radical copolymerization[14−17] between maleimide-ended oligomonomers and limonene. We are currently synthesizing sequence-regulated vinyl copolymers possessing three controlled monomer sequences and/or sequenced functions in the side chains as well as 1:2-monomer sequences in the main chains and investigating the effects of the sequences on the polymer properties, structures, and functions. The monomer sequence control in both main and side chains is thus expected to contribute to further development of designing synthetic polymers as well as clarifying the importance of sequence regulation on the polymer properties.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details and supplementary data are included. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsmacrolett.5b00379.

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Notes

The authors declare no competing financial interest.

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