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Low-Temperature Polymerization of endo- and exo-2-Methyl-7-oxabicyclo-[2.2.1]-heptane

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ABSTRACT

Polymerization of the title compounds in methylene dichloride with PF_5 catalyst have shown that the rate of polymer formation drops sharply with temperature and the polymerization ceases entirely around -60 to -70°C. Experiments carried out with the exo-2-Me isomer have shown that at -30°C a limiting conversion of approx 40% is attained and simultaneously the molecular weight and the molecular weight distribution level off. At -50°C the same limiting conversion level is reached; however, the molecular weight level is higher and a study of changes in molecular weight distribution with time indicates that at this temperature a greater proportion of chains remain active throughout the polymerization. Even at -30°C, however, experiments with changing conditions, especially the temperature, during the runs have demonstrated that the systems are not "dead" after the limiting conversion has been reached. Polymerization of the endo-2-Me isomer at -50°C has shown that in the time interval studied the limiting viscosity number increases essentially linearly with time.

INTRODUCTION

The polymerization of endo- and exo-2-methyl-7-oxabicyclo-[2.2.1]-heptane was first studied by Wittbecker and co-workers [1]. Later studies were conducted by Guisti et al. [2-4] in connection with the utilization of different catalytic systems and generally at temperatures in the 0 to 35°C range. We have recently studied the polymerization of these two isomers along with other methyl-substituted derivatives at lower temperatures using PF_5 catalyst and with the main objective of elucidating the mechanism of the ring-opening steps in these polymerizations [5]. With regard to the effect of temperature, we observed an increase in both yield and molecular weight with decreasing temperature in the +25 to -30°C range; however, at -78°C no polymerization took place. In a recent paper by Guisti et al. [6] on the polymerization of exo-2-methyl-7-oxabicyclo-[2.2.1]-heptane under the influence of PF_5 catalyst brief mention was made of some apparently preliminary results carried out in the 0 to -30°C range. It was found by this group that quantitative yields of polymer could be obtained in this temperature range, and it was proposed that the polymerization systems under these conditions are of a "living nature" since a second addition of monomer polymerized completely. However, there was no increase in the molecular weight; on the contrary, it seemed to decrease.

In the present paper data will mainly be presented which will fill the gap between -30 and -78°C which was not covered in our previous studies, and the nature of the system will be discussed in relation to the polymerization temperature.

EXPERIMENTAL

Materials

The two isomeric monomers were prepared in accordance with the previously published method [1] and by repeated distillation on a spinning band column were obtained as pure fractions.

endo-2-Methyl-7-oxabicyclo-[2.2.1]-heptane: Purity by gas-liquid chromatography > 99.7%, $n_D^{25} = 1.4442$.

exo-2-Methyl-7-oxabicyclo-[2.2.1]-heptane: Purity by gas-liquid chromatography > 99.8%, $n_D^{25} = 1.4494$.

Methylene dichloride (Merck pro analysis, 99.5%) was used as solvent in all the experiments and it was stored over barium oxide prior to use.

PF_5 catalyst was generated by decomposing benzenediazonium hexafluorophosphate (Ozark Mahoning Co., Tulsa, Oklahoma).

Polymerization Procedure

The polymerization were carried out in connection with the use of a high vacuum line operated at pressures below 2×10^{-5} Torr and a polymerization technique utilizing breakseals as described elsewhere [5]. The polymers were recovered by precipitation in methanol (tenfold excess) followed by thorough washing with dilute bicarbonate solution, water, and methanol before final drying in vacuo at 50° C.

All the polymerization experiments were carried out using a monomer concentration of 1.40 moles/liter and a catalyst concentration of 0.056 mole/liter (based on the liquid phase).

Characterization

Limiting viscosity numbers were determined for the polymers of the endo-2-Me isomer in m-cresol at 25° C using an Ubbelohde viscometer in connection with a Hewlett-Packard autoviscometer for photoelectric registration of the elution times.

The polymers of the exo-2-Me isomer were soluble in common solvents and were analyzed by GPC in THF solvent. A Waters model 200 instrument equipped with polystyrene gel-columns (porosities: 10^3, 10^4, 2×10^4, and 10^6 Å) was used. On the basis of a calibration curve obtained with narrow molecular weight polystyrenes, molecular weight average values were calculated via the average exteded chain lengths and the use of a Q-value (weight per Å) of 18.4. The molecular weight values obtained in this fashion are most likely not the true ones; however, they are adequate for assessing the influence of the parameters on the polymerization process.

RESULTS AND DISCUSSION

Polymerization experiments have been carried out with both the endo- and exo-2-methyl-7-oxabicyclo-[2.2.1]-heptane covering the -30 to -78° C range which was not covered in our previous studies [5]. The data are presented in Tables 1 and 2 and discussed on the basis of the various appropriate plots.

For a fixed reaction time (90 hr) it is evident from Fig. 1 that the increase in yield which was found previously upon decreasing the reaction temperature down to -30° C is followed by a sharp drop in yield when the temperature is lowered still further. At -60° C a yield of 0.8% was obtained for the endo-2-Me isomer while it was zero for the exo-2-Me isomer. These results are in agreement with our previous observations that neither of the two isomers polymerized at

TABLE 1. Polymerizations of exo-2-Methyl-7-oxabicyclo-[2.2.1]-heptane[a]

Temp (°C)	Time (hr)	Yield (%)	GPC[b] $\overline{M}_n$	$\overline{M}_w$	$\overline{M}_w/\overline{M}_n$	Remarks
-60	90	0				
-50	45	2	2,500	2,980	1.19	
-50	90	9	4,030	5,310	1.32	
-50	160	19	6,790	9,440	1.39	
-50	283	41	9,860	14,880	1.51	
-50	425	39	11,090	20,030	1.80	
-50	550	40	10,360	17,130	1.66	
-40	90	30	9,350	15,800	1.70	
-30	5	10	3,300	4,250	1.29	
-30	10	19	4,750	6,710	1.41	
-30	19	21	6,100	10,650	1.75	
-30	48	28	6,360	12,320	1.94	
-30	90	35	6,730	12,570	1.87	
-30	184	41	6,550	12,280	1.88	
-30	288	42	6,400	12,730	1.99	
-30	284	53	6,810	14,700	2.16	After 166 hr a second portion of monomer was added
-30	334	61	5,430	11,000	2.03	After 166 hr a second portion of catalyst was added
-30	279	58	4,700	10,000	2.13	After 171 hr the temperature was changed to 0°C
-30	310	57	5,110	10,420	2.04	After 168 hr the temperature was changed to -15°C

[a] In each experiment the monomer concentration was 1.4 moles/liter in methylene dichloride and the catalyst concentration 0.056 mole/liter.

[b] The calculated values are based on extended chain lengths using a Q-value (weight per Å) of 18.4.

TABLE 2. Polymerization of endo-2-Methyl-7-oxabicyclo-[2.2.1]-heptane[a]

Temp (°C)	Time (hr)	Yield (%)	Limiting viscosity No.[b] (dl/g)	Remarks
-60	90	0.8	-	
-50	41	3.9	1.05	The polymer precipitates
-50	63	12	1.18	" " "
-50	90	24	1.38	" " "
-50	161	21	2.09	" " "
-50	168	23	2.10	" " "
-50	239	35	2.74	" " "
-40	90	76	2.50	" " "

[a] In each experiment the monomer concentration was 1.4 moles/liter in methylene dichloride and the catalyst concentration 0.056 mole/liter.

[b] Determined in m-cresol at 25°C.

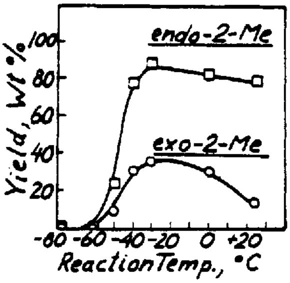

FIG. 1. Yield of polymer after 90 hr at different reaction temperatures.

-78°C. We have now also studied how the yield depends on the reaction time, and in Fig. 2 the results obtained for the exo-2-Me isomer at two different temperatures are illustrated. At -30°C a rapid increase in yield takes place during the first 24 hr of reaction, but upon extending the reaction time a limiting conversion of around

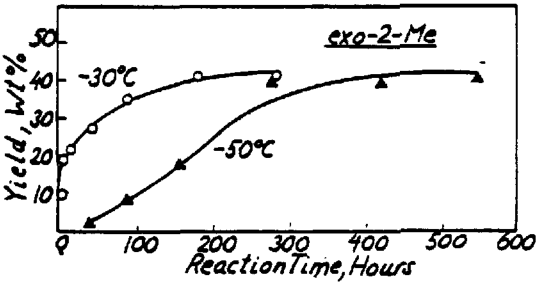

FIG. 2. Yield of polymer vs reaction time.

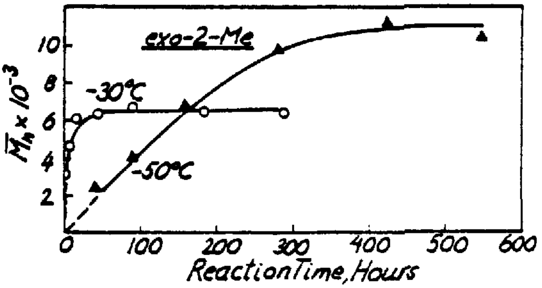

FIG. 3. Number-average molecular weight vs reaction time.

40% is gradually reached. At the lower temperature, -50° C, however, there is first a gradual increase in the yield up to 40% which is reached after approx 300 hr, after which the yield remains constant while the reaction time is almost doubled. It is seen that the limiting yield value of around 40% at -50° C coincides with that obtained at -30° C. The plot in Fig. 1 is obviously only valid for the particular reaction time which was selected as a standard condition in the initial studies.

The increase in molecular weight as a function of time was also determined, and in Fig. 3 it is seen that the number-average molecular weight at -30° C during the first 24 hr of reaction reaches a plateau value, while the molecular weight at -50° C increases much more gradually and eventually appears to attain a plateau value which, however, is appreciably higher than that attained at -30°. On the basis of the GPC analyses which were performed on all the polymers, the change in molecular weight distribution could also be followed and the polydispersity was expressed by the index $\overline{M}_w/\overline{M}_n$. The values obtained are

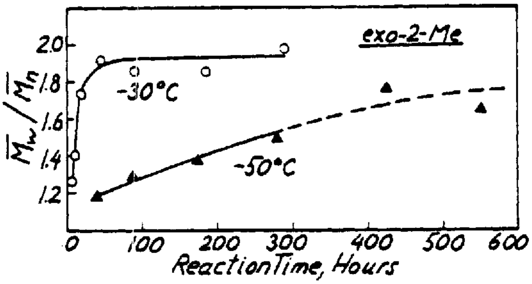

FIG. 4. Polydispersity index vs reaction time.

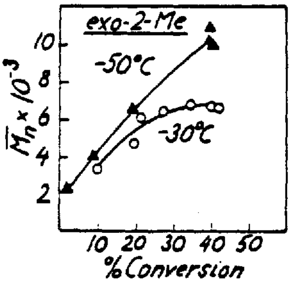

FIG. 5. Number-average molecular weight vs conversion.

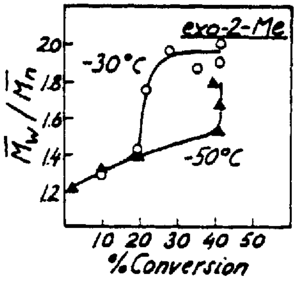

FIG. 6. Polydispersity index vs conversion.

shown in Fig. 4, and from this it is obvious that the polydispersity generally is lower for the polymers prepared at the lowest temperature. For the polymers prepared at -30°C it may be seen that a constant value for the polydispersity index close to 2.0 is reached as the molecular weight becomes constant when the yield start to approach the limiting value. The polydispersity index for the polymers prepared at -50°C increases very gradually with time and, after the molecular weight reaches a constant value (Fig. 3), the polydispersity index should also be expected to become constant at some point. However, scatter in the data plotted in Fig. 4 makes it somewhat uncertain if such a constant value is reached within the maximum reaction time investigated here.

It is useful also to consider how the molecular weight and the molecular weight distribution changes with conversion, and these changes may be seen in Figs. 5 and 6. It is apparent from Fig. 5 that the molecular weight at any degree of conversion is higher for the polymer prepared at the lower reaction temperature. From Fig. 3 it may be seen, however, that the polymer prepared at this lower temperature (-50°C) may well have a molecular weight which is lower than that of the polymer prepared at -30°C after a certain reaction time, but due to the large difference in the rate of conversion at the two temperatures the appearance of plot in Fig. 3 changes appreciably when the molecular weight as a function of conversion is considered. The polydispersity index is, as seen in Fig. 6, rather similar at low conversion for the polymers prepared at the two temperatures. However, at approx 20% conversion the distributions for the polymers prepared at -30°C become much broader. As already mentioned, this occurs when the yield starts to taper off toward the plateau value. It is also seen for the polymers prepared at -50°C that the polydispersity increases more markedly when the constant value of the yield is approached at that temperature. A polymerization carried out at -40°C to 30% conversion yielded a polymer with a polydispersity index of 1.70 (see Table 1). From Fig. 6 it may be seen that this value is very close to the mean of the values expected for polymers prepared at -30 and -50°C, respectively, at this conversion.

The molecular weight distributions are more closely examined by considering the actual GPC distribution curves. In Fig. 7 the distributions are shown for the four experiments at -50°C for which a gradual increase in yield and molecular weight to plateau values were observed. These curves have been constructed by first performing a normalization with respect to the amount of material used for the analysis (i.e., to equal sums of heights in the GPC chromatograms) and then adjusting the areas under the curves in accordance with the actual yields. In Fig. 8 the curves of Fig. 7 which represent the weight distribution have been transformed into frequency distributions by dividing the heights in the chromatograms by the corresponding molecular weights. It is obvious from these various curves that the amount of material in the

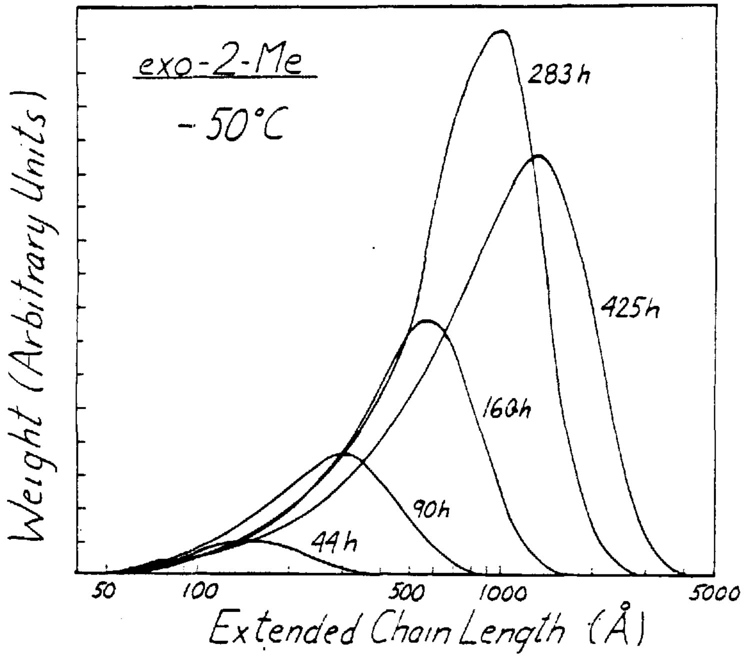

FIG. 7. Weight distribution of extended chain lengths after different reaction times at -50°C.

very low molecular weight end corresponding to that positioned under the curve for the polymer with the lowest conversion is roughly constant. Consequently the polymerization does not progress solely by addition of monomer units to initially formed active species. As time progresses the curves in Fig. 8, however, indicate shifts of the lower molecular weight species toward higher molecular weight species. It was already pointed out that the polydispersity index is relatively low, below 1.5, for the polymers prepared during the period with increasing yield at -50°C, indicating that the chain length distribution is not governed by a random process. The frequency distribution curves for polymers prepared at -30°C, however, do not show as clear a progression toward higher molecular weight values with time as for the polymers prepared at -50°C as may be seen on Fig. 9.

The rate of initiation appears to be rather fast compared to the rate of propagation at both temperatures as judged by the relatively narrow molecular weight distribution during the early stages of conversion (Fig. 6). For the same reason termination or transfer is probably not prevalent during this period. Upon extending the time of reaction the

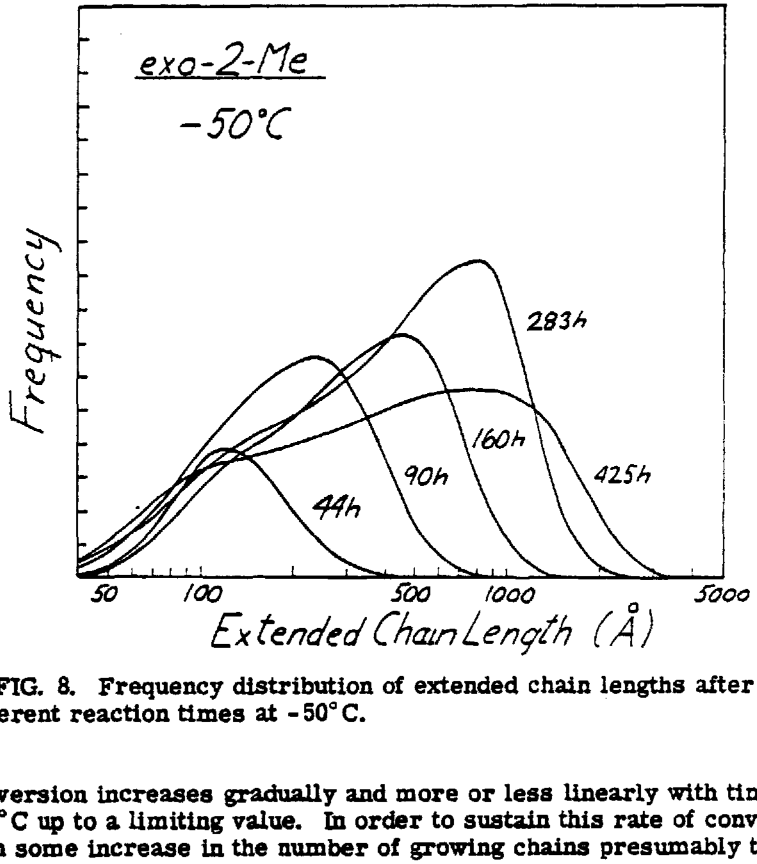

FIG. 8. Frequency distribution of extended chain lengths after different reaction times at -50° C.

conversion increases gradually and more or less linearly with time at -50° C up to a limiting value. In order to sustain this rate of conversion some increase in the number of growing chains presumably takes place. This continued initiation of chain growth and perhaps, some termination lead to some broadening of the molecular weight distribution although it remains relatively narrow. A proportion of the chains appears to continue its growth over long time intervals, particularly at the lowest reaction temperature as indicated by the distribution curves in Figs. 7 and 8. At -30° C a leveling occurs rather early with respect to molecular weight and molecular weight distribution, and gradually with respect to the conversion. The broadening of the molecular weight distribution occurs mainly after approx 20% conversion. The leveling effect and the marked increase in the polydispersity index could be due to the approach to an equilibrium between monomer and polymer, as has been found in the polymerization of THF [7]. However, in the present case a true equilibrium may not be reached.

In order to investigate this question, experiments were performed where the reaction conditions were changed after a limiting conversion

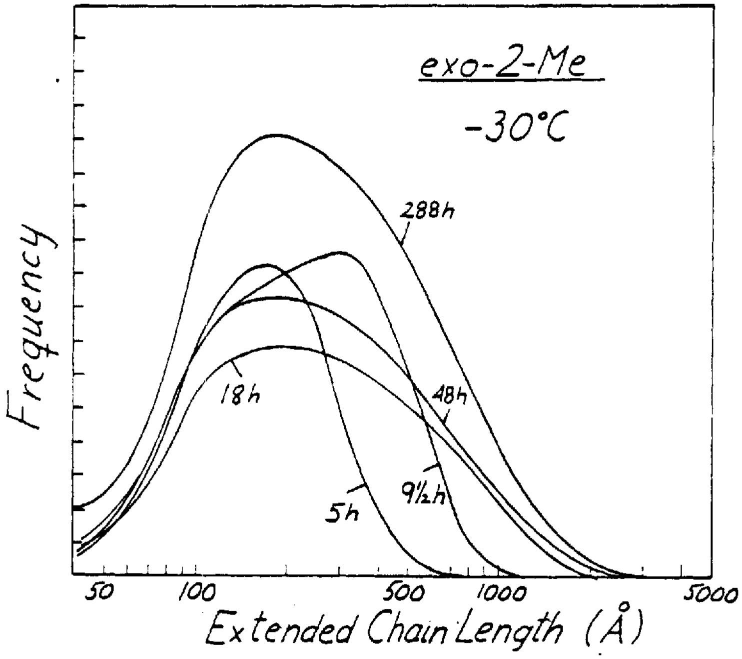

FIG. 9. Frequency distribution of extended chain lengths after different reaction times at -30° C.

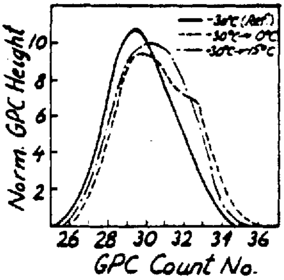

FIG. 10. Molecular weight distribution upon changing the reaction temperature after approximately 165 hr at -30° C.

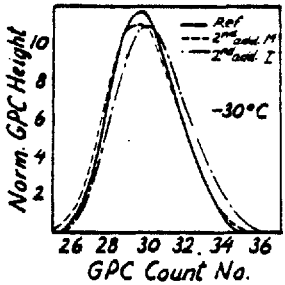

FIG. 11. Molecular weight distribution upon adding a second portion of monomer (M) and catalyst (I).

of approx 40% had been reached after 165-170 hr of reaction at -30°C. In Fig. 10 is seen the changes in MWD upon changing the reaction temperature. After approx 100 hr at 0°C a bimodal distribution was obtained and this result did not change after doubling the reaction time. A change from -30°C to only -15°C resulted in a polymer with a distribution intermediate between the reference curve at -30°C and that obtained after changing the temperature to 0°C. The yields increased to around 56-58% after reaction at the higher temperature. By changing the temperature from -30 to -50°C, however, no significant change in yield or molecular weight could be detected.

The results of the addition of a second portion of monomer or catalyst, corresponding in each case to the quantity used from the start, is seen in Fig. 11. The MWD's are shifted somewhat toward higher and lower molecular weight values, respectively. The yield in the case of a second addition of monomer increased from approx 40 to 53% based on the initial monomer charge. A second addition of catalyst resulted in an increase in yield from the approx 40 to 61%.

These experiments where the polymerization conditions were changed indicate that the system is not "dead" when the plateau value of conversion is reached at -30°C; however, the resulting changes are limited and, for example, only a minor fraction of the additional monomer will polymerize. A true equilibrium situation is probably not attained due to the occurrence of gradual termination at this temperature. As already discussed, however, at lower temperatures the chain growth is sustained for long periods and under these conditions the system may more closely resemble a "living polymer system." The nature of the system may resemble that of oxepane for which a strongly temperature-dependant gradual decrease in the concentrations of active species was observed [8]. Experiments with second additions have not yet been carried out at temperatures below -30°C.

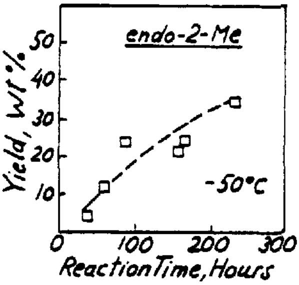

FIG. 12. Yield of polymer vs reaction time.

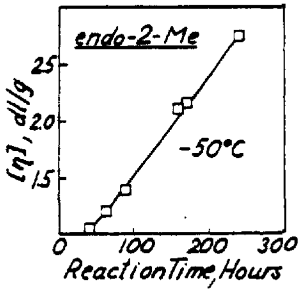

FIG. 13. Limiting viscosity number vs reaction time.

Finally, some experiments with the endo-2-Me-isomer shall briefly be mentioned. In Figs. 12 and 13 is seen that both the yield and the limiting viscosity number increases with the reaction time at -50°C. Considerable scatter may be noted in the yield data, and this may be associated with the fact that in these polymerizations the polymer precipitates and after approx 15% conversion the system becomes immobile. At -60°C the rate of polymerization is very slow, but at -50°C the polymerization progresses and the steady increase in limiting viscosity number (Fig. 13) matches the increase in molecular weight with time for the exo-2-Me isomer at the same temperature. For both isomers the active species in the polymerizations seem to have considerable lifetimes when the reaction is carried out at very low temperatures.

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