of the backbone. However, inspection of Table II shows precisely the opposite trend for i·(i + 3) interactions.

Even a basically linear protein structure such as tropomyosin's is rife with possible combinations. One can see examples in it of just about anything one wishes. Under the circumstances, it is probably most practical to focus upon those that satisfy some appropriate criterion other than the fact of their existence. It has not been demonstrated that intrahelical salt linkages pass any such test.

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(12) We include *all* potential ion pairs. For example, glutamate-33, which has a lysine at 33 + 4 = 37 *and* another lysine at 33 − 4 = 29, contributes two pairs of potential i·($i \pm 4$) attractive pairs to the total number. The total obtained in the following paragraph for i·($i \pm 4$) attractive pairs that involve glutamate was obtained on the same basis.
(13) The factor of 2 is a bit too large. It only holds for an interior glutamate residue, i.e., one that *has* a neighbor at both $i - 4$ and $i + 4$. Thus, only residue positions 5–280 would qualify. A glutamate in positions 1–4 would only have one such neighbor (at $i + 4$) and one in positions 281–284 would also have only one such neighbor (at $i - 4$). Thus, the average number of such neighbors per residue is [(2)(276) + 8]/284 = 1.972. Use of this factor instead of 2 gives an expectation value of 21.4 instead of 22, an immaterial change.
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Influences of the Initiation and Termination Reactions on the Molecular Weight Distribution and Compositional Heterogeneity of Functional Copolymers: An Application of Monte Carlo Simulation

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ABSTRACT: Monte Carlo simulations have been used to predict the molecular weight, molecular weight distribution, and composition of copolymers. The method is particularly suited to the simulation of copolymerizations carried out in the presence of chain-transfer agents (e.g., thiols). Calculations have been performed to show that selectivity shown in the initiation and termination reactions can have a dramatic influence on the composition and molecular weight distribution of cooligomers and copolymers.

Introduction

The aim of this work has been to examine the factors that determine the composition and molecular weight distribution of multicomponent copolymers, in particular, to discover what influences selectivity shown in the initiation and termination steps might have on the distribution of monomer units within the copolymer chain. This is of particular relevance in the synthesis of functional copolymers and cooligomers, which find widespread use in the coatings and adhesives industry.[1,2]

That such considerations should be of significance, particularly where low molecular weight materials are concerned, can be readily appreciated given the knowledge that initiator and transfer agent derived radicals can show a high degree of selectivity for reaction with a given monomer.[3] Thus the initiating end of the polymer or oligomer

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chain need not be representative of the overall structure. Similarly, if one examines tabulations of transfer constants[4] or considers the kinetics of copolymerizations involving radical–radical termination,[5] one finds that the probability for termination of a given chain has a marked dependence on the nature of the last added monomer unit. With these factors in mind, it then also becomes important to evaluate the dependence of the compositional heterogeneity on the nature of the monomers employed.

While spectroscopic techniques or chemical analysis can tell us the average composition, and in some cases NMR may give the average sequence distribution, there are at this stage no reliable experimental procedures for examining the compositional heterogeneity of copolymers or cooligomers. The approach used to circumvent this problem has been to calculate the structure of copolymers on the basis of rate data available in the literature. The information thus obtained can then be applied in advancing our understanding of copolymer properties and in designing further experiments.

Stockmayer[6] was one of the first to report on the problem of compositional heterogeneity and presented formulas for calculating the instantaneous copolymer composition as a function of chain length. Fueno and Furukawa[7] and Mirabella[8] also examined the variation in copolymer composition with chain length, the latter looking at the cumulative copolymer composition by Monte Carlo simulation. Both groups took into account only the initiation and propagation reactions. They showed that for short chains the initiation reaction could have a significant influence on composition but lacked the experimental data on which to base a more detailed investigation.

More recently, O'Driscoll[9] has used Monte Carlo simulation to examine the compositional heterogeneity of binary and ternary copolymers. He realized that both the initiation and termination reactions could influence the compositional heterogeneity, but still assumed no particular selectivity in these steps, using the argument that to do so would take one beyond the present stage of knowledge in these areas. While it is true that much of the specific rate data required are not yet available, there is sufficient (see below) to (a) demonstrate that there is significant selectivity in the initiation and termination reactions, (b) enable the influences of the above-mentioned factors to be reasonably examined, and (c) show that ignoring such factors could lead to significant errors in the calculated structure.

The systems chosen for detailed study are low molecular weight terpolymers of hydroxyethyl acrylate (HEA) or methacrylate (HEMA) with styrene and butyl acrylate (BA) which are polymerized in the presence of an added thiol as transfer agent for molecular weight control.

Rate Constants and Reactivity Ratios

There are no relative rates of initiation by sulfur-centered radicals or transfer constants to thiols specific to HEA or HEMA polymerization available in the literature. Accordingly, the rate data for the corresponding methyl esters were used. The relative initiation rates by alkylthiyl radicals employed are those determined by Sato and Otsu for initiation by phenylthiyl radical.[10] Transfer constants (C_{Ti}) used are those for butanethiol (see Table I).

Despite an extensive search of the recent literature we were unable to find reactivity ratio data that had been obtained under a consistent set of reaction conditions. However, our survey did establish that the reactivity ratios were very much dependent on reaction conditions (Table II). Therefore, in order to have a consistent set of reactivity ratios, these were estimated from the most recent

Table I
Values of Relative Rate Constants for Initiation [k_I(rel)], Transfer Constants (C_T), and Q–e Values

monomer	k_I(rel)[a]	C_T[b]	Q	e
hydroxyethyl acrylate	0.32[c]	1.69[c]	0.82	0.68[13]
hydroxyethyl methacrylate	1.0[d]	0.66[d]	1.78	−0.39[12]
butyl acrylate	0.32[c]	1.69[c]	0.41	1.06[11]
styrene	12.0	22.0	1.00	0.80

[a] Relative rate constant for initiation by phenylthiyl radical.[10] [b] Transfer constant to butanethiol.[4] [c] Value for methyl acrylate (see text). [d] Value for methyl methacrylate (see text).

Table II
Reactivity Ratios

M_1	M	r_{12}	r_{21}
hydroxyethyl acrylate	butyl acrylate[a]	2.684	0.322
	butyl acrylate[b]	0.94	0.23
	butyl acrylate[c,9]	1.08	0.94
	styrene[a]	0.311	0.360
	styrene[d]	0.34	0.38
	styrene[c,9]	0.24	0.70
hydroxyethyl methacrylate	butyl acrylate[a]	2.466	0.050
	butyl acrylate[e]	4.764	0.086
	styrene[a]	2.089	0.405
	styrene[f]	0.856	0.332
	styrene[g]	0.87	0.16
	styrene[h]	0.538	0.442
	styrene[i]	1.65	0.50
	styrene[j]	0.59	0.53
butyl acrylate	styrene[a]	0.057	0.551
	styrene[c,11]	0.2	0.76

[a] Calculated from Q–e values given in Table I. [b] Bulk, 60 °C (Catala, J. M.; Nonn, A.; Pujol, J. M.; Brossas, J. *Polym. Bull. (Berlin)* **1986**, *15*, 311). [c] No conditions stated. [d] Benzene, 60 °C (Chow, C. D. *J. Polym. Sci., Polym. Chem. Ed.* **1975**, *13*, 309). [e] Bulk, 60 °C, data of Varma et al. (Varma, I. K.; Patnaik, K. *Eur. Polym. J.* **1976**, *12*, 259) recalculated by Greenley,[12] who quotes an incorrect reference. The temperature dependence of r_{12} has also been examined (Varma, I. K.; Patnaik, K. *Eur. Polym. J.* **1977**, *13*, 175). [f] Bulk, 60 °C, data from Okano et al. (Okano, T.; Aoyagi, J.; Shinohara, I. *Nippon Kagaku Kaishi* **1976**, 161) recalculated by Greenley.[12] [g] 1:1 xylene–ethane-1,2-diyl diacetate solvent, 95 °C (Probst, J.; Kolb, G. *Angew. Makromol. Chem.* **1981**, *98*, 195). [h] DMF, 50 °C, data from Noma et al. (Noma, K.; Niwa, M.; Iida, S.; Nakaazato, Y. *Kobunshi Robunshu (Engl. Ed.)* **1975**, *4*, 244) recalculated by Greenley.[12] [i] 1-Butanol or 2-propanol solvent, 80 °C (Lebduska, J.; Snuparek, J., Jr.; Kaspar, K. *J. Polym. Sci., Polym. Chem. Ed.* **1986**, *24*, 777.). [j] DMF or toluene solvent, 80 °C (ref given in footnote I).

Q–e values (see Table I)[11-13] according to the expression $r_{ij} = Q_i/Q_j \exp[-e_i(e_i - e_j)]$.

Although the applicability of the kinetic parameters given in Table I may be questioned at some future time as more relevant experimental data become available, their use does not detract from the general conclusions we wish to draw.

Method

In circumstances where penultimate group effects can be neglected, the reaction scheme for multicomponent copolymerization in the presence of a transfer agent (RSH) may be represented schematically as follows.

initiation:

$$\mathrm{RS}^\bullet + \mathrm{M}_1 \xrightarrow{k_{I1}} \mathrm{M}_1^\bullet$$

$$\mathrm{RS}^\bullet + \mathrm{M}_2 \xrightarrow{k_{I2}} \mathrm{M}_2^\bullet$$

$$\mathrm{RS}^\bullet + \mathrm{M}_i \xrightarrow{k_{Ii}} \mathrm{M}_i^\bullet \qquad (1)$$

propagation:

$$\begin{aligned} M_1^\bullet + M_1 &\xrightarrow{k_{11}} M_1^\bullet \\ M_1^\bullet + M_2 &\xrightarrow{k_{12}} M_2^\bullet \\ &\vdots \\ M_2^\bullet + M_1 &\xrightarrow{k_{21}} M_1^\bullet \\ &\vdots \\ M_i^\bullet + M_j &\xrightarrow{k_{ij}} M_j^\bullet \end{aligned} \quad (2)$$

transfer:

$$\begin{aligned} RSH + M_1^\bullet &\xrightarrow{k_{T1}} RS^\bullet + M_1H \\ RSH + M_2^\bullet &\xrightarrow{k_{T2}} RS^\bullet + M_2H \\ &\vdots \\ RSH + M_i^\bullet &\xrightarrow{k_{Ti}} RS^\bullet + M_iH \end{aligned} \quad (3)$$

where $i, j = 1$–n, and n is the number of components in the copolymerization.

In our simulation initiation by initiator-derived radicals and termination by radical–radical reactions have been neglected. This corresponds to the usual experimental conditions of low initiator and high transfer agent concentrations when the proportion of chains affected by such processes is small.

From a consideration of the above reaction scheme the following relationships (eq 4–7) can be derived.

$$\sum P(I|i) = 1.0 \quad (4)$$

where $P(I|i)$ is the conditional probability that an initiating species ($RS^\bullet$) will add to monomer M_i. If the initiation step is not rate-determining, the initiation probabilities are proportional to the relative values of the initiation rate constants k_{Ii}(rel) (see Table I).

$$P(i|i) = \frac{1.0}{1.0 + \sum_j \left(\frac{[M_j]}{[M_i]} \frac{1}{r_{ij}} \right) + \frac{[RSH]}{[M_i]} C_{Ti}} \quad (5)$$

$$P(i|j) = P(i|i) \frac{[M_j]}{[M_i]} \frac{1}{r_{ij}} \quad (6)$$

$$P(i|T) = P(i|i) \frac{[RSH]}{[M_i]} C_{Ti} = 1.0 - \sum_j P(i|j) \quad (7)$$

where $P(i|j)$ is the conditional probability that a chain ending in monomer M_i will add monomer M_j and $P(i|T)$ is the conditional probability that a chain ending in monomer M_i will terminate by chain transfer. Note that $r_{ij} = k_{ii}/k_{ij}$ and $C_{Ti} = k_{Ti}/k_{ii}$.

A variety of programs have appeared in the literature for the implementation of a Monte Carlo simulation of copolymerization. However, none treat both the initiation and termination reactions satisfactorily. We have therefore written programs in standard Fortran 77 to run on Cyber 840, 205, or Microvax 2 computers which simulate copolymerizations involving 2–4 components and enable the calculation of copolymer composition and sequence and molecular weight distribution with the following options: (a) constant monomer composition; (b) allowing the monomer composition to vary as monomer is incorporated into the polymer chain; (c) as (b) but allowing for incremental addition of monomer after a chosen number of monomer addition steps. Programs have also been written that allow the influence of penultimate group effects on the reactivity ratios to be taken into account. In this paper we consider only the instantaneous composition of copolymers (i.e., option a). Studies planned or in progress are aimed at predicting the cumulative composition of multicomponent copolymers to high conversion.

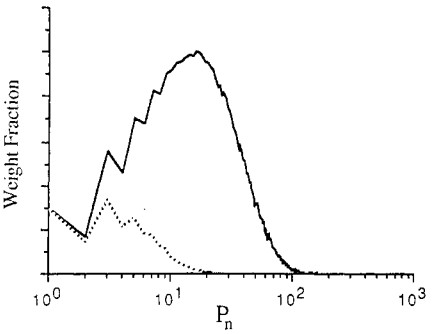

Figure 1. Calculated weight fraction vs. degree of polymerization for a HEA:BA:styrene (20:40:40) copolymer prepared in the presence of a thiol chain-transfer agent. $\bar{P}_n = 15$ and polymerization according to eq 1–3. See column 1, Table III. The upper trace is the overall molecular weight distribution, and the lower trace is the distribution of chains not containing HEA.

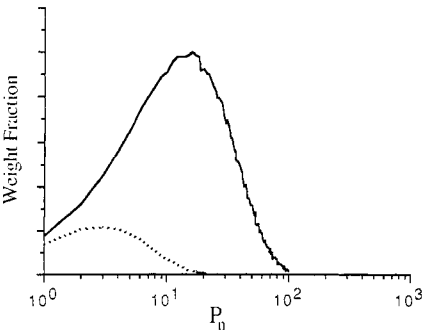

Figure 2. Calculated weight fraction vs. degree of polymerization for HEA:BA:styrene (20:40:40) copolymer with $\bar{P}_n = 15$ and assuming equal initiation and equal termination rates. See column 2, Table III. The upper trace reflects the overall molecular weight distribution, while the lower trace is the distribution of chains not containing HEA.

We used the above-mentioned programs to evaluate the overall molecular weight distribution and the distribution of chains containing exactly 0, 1, and 2 units of a given monomer. The average degrees of polymerization ($\bar{P}_n$) were also calculated. Figures 1 and 2 and Table III show the results of our calculations. A total of 5 000 000 iterations (additions of monomer) were performed for each calculation. Note, however, that after only 500 000 iterations the parameters given in Table III are within 2% of the values shown. The larger number of iterations was required only for purposes of obtaining a reasonably "noise-free" weight distribution plot.

Discussion

One of the more important applications of functional copolymers is in the coatings and adhesives industry where such materials are used as macromonomers in the production of cross-linked resins. In these circumstances it is vital to know and be able to control the degree of functionality of the functional copolymers. The reasons for this are as follows. Chains that do not contain the functional monomer (HEA or HEMA) cannot become incorporated into a cross-linked system. Chains with a single unit of the functional monomer can become incorporated

Table III
Calculated Composition of Terpolymer Prepared with Monomer Feed Ratio [M_1]:[BA]:[Styrene] = 20:40:40

functional monomer (M_1)	HEA	HEA[a]	HEA	HEA[a]	HEMA	HEMA
[T][b]	1.0		0.2		1.0	0.2
overall $\bar{P}_n$	15.0	15.0	71.1	70.6	18.6	88.9
% M_1 in copolymer	20.5	21.6	21.6	21.9	32.0	33.3
% BA in copolymer	24.3	26.6	25.5	26.0	26.6	27.7
% styrene in copolymer	55.2	51.7	52.8	52.1	41.3	39.0
% chains $P_n = 1$	11.1	6.7	2.4	1.4	11.3	2.4
% chains $P_n = 2$	3.1	6.2	0.8	1.3	3.2	0.7
% chains $P_n = 3$	6.9	5.8	1.8	1.3	4.8	1.2
$\bar{P}_n$ chains with zero M_1	3.2	3.5	3.7	4.1	2.4	2.7
weight percent	5.5	4.5	0.35	0.27	2.7	0.16
mole percent	26.1	19.1	6.6	4.7	21.5	5.2
$\bar{P}_n$ chains with one M_1	7.3	6.2	8.6	7.4	6.1	6.7
weight percent	8.5	8.4	0.69	0.62	3.4	0.22
mole percent	17.6	20.2	5.7	5.9	10.4	2.9
$\bar{P}_n$ chains with two M_1	11.0	10.1	12.8	11.7	8.6	9.7
weight percent	9.9	10.1	0.96	0.88	4.2	0.32
mole percent	13.5	15.1	5.3	5.4	8.8	3.0

[a] Calculated assuming equal initiation rates and a monomer-independent termination probability chosen so as to give the required P_n. [b] Relative to total monomer concentration (=100.0).

but only by consuming a possible cross-linking site in a copolymer chain of higher functionality, and in doing so they create chain branches. Chains with two functional monomer units cannot directly act as cross-linking agents; they simply extend the chain or branch length.

It is clear from Figure 1 and Table III that for the systems studied, there is a marked preponderance of chains with an odd number of monomer units. Furthermore, by comparing the results shown in Figures 1 and 2, one can see that this occurs as a result of selectivity in the initiation and termination reactions.

The results may be interpreted as follows. The thiyl radical has a preference to add to styrene over HEA, HEMA, or BA (see Table I), and there is a tendency for alternation between addition of styrene and the acrylic monomers. Thus the first unit in every chain is likely to be styrene, the second acrylate or methacrylate, the third styrene, and so on. In relation to the competing propagation reactions those chains ending in styrene have a greater reactivity (Table I) toward thiol than those chains with an acrylic monomer as the terminal unit. Therefore, chains containing an odd number of monomer units have a greater probability of undergoing termination by chain transfer. These effects are most pronounced for low molecular weight chains since the influence of the initiating species ($RS^\bullet$) on the copolymer composition is damped out with increasing chain length.

The above-mentioned factors have a number of other important consequences, including the following:

(a) The copolymer will contain a greater fraction of styrene and a lower fraction of HEA, HEMA, and BA than would be predicted on the basis of the reactivity ratio data alone (see Table III). This effect is most noticeable when chains of low molecular weight are being produced.

(b) In higher molecular weight copolymers the sequence distribution of chain ends will not be representative of the overall sequence distribution. This is a consequence of the selectivity shown in the initiation and termination reactions, which results in the initial and final unit of every chain being, most likely, a styrene unit.

(c) The copolymer will contain a relatively high fraction of one-unit (styrene) chains (see Table III).

It may be possible, or indeed desirable, to make use of this behavior. For example, it may used to advantage in circumstances where a high degree uniformity in terminal functional groups is desired. There is the possibility of selecting not only the end groups but also the type of terminal monomer units present in copolymer chains by appropriate choice of transfer agent. There is, however, a need for further work aimed at establishing the relative rates of initiation by transfer agent derived radicals.

The findings reported here are also relevant to copolymerizations carried out in the absence of transfer agent where termination occurs by radical–radical reactions. We have previously shown that there is significant selectivity in this process and that, for example, in styrene–methyl methacrylate copolymerization most termination events will involve styryl–styryl interaction.[5] However, simulation of copolymerizations that involve termination by radical–radical reactions require values for the absolute rate constants for termination and propagation that are less readily available and are, as a rule, less reliable and a decision regarding the factors influencing termination about which there remains some controversy.[5]

Finally attention should be drawn to the differences in composition between copolymers prepared with HEA as opposed to HEMA as the functional monomer. The HEMA copolymer shows the above-mentioned anomalies to a significantly lesser extent, largely as a result of the reduced tendency for alternation between styrene and HEMA.

Conclusions

Multicomponent copolymerizations carried out in the presence of a chain-transfer agent (eq 1–3) are ideally suited to analysis by Monte Carlo simulation since actual molecular weights and compositions can be calculated on the basis of relative rate data (initiation rates, reactivity ratios, and transfer constants) which are available in the literature or are measurable by standard techniques. These calculations show that nature of the initiation and termination reactions can have a profound influence on the molecular weight and composition of copolymers. The effects are most noticeable for low molecular weight copolymers. Experiments aimed at verifying these phenomena are in progress.

Registry No. HEA, 818-61-1; HEMA, 868-77-9; BA, 141-32-2; (HEA)(BA)(styrene) (copolymer), 26587-25-7; (HEMA)(BA)(styrene) (copolymer), 26916-03-0; styrene, 100-42-5.

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Cooperative Relaxations in Condensed Macromolecular Systems. 1. A Model for Computer Simulation

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ABSTRACT: A microscopic model of cooperative relaxations in condensed macromolecular systems is proposed. The mechanism suggested consists in collective replacement of molecular subsegments within closed loops of motion. The model is applied to computer simulations of chain motions on a lattice with all sites occupied. Examples of computer experiments based on melting of regular structures with linear and ring chains are shown. Final isotropic amorphous systems that are completely filled with ideal randomly coiled chains have been obtained. Chain lengths were varied between 16 and 1024 chain segments.

Introduction

The molecular motion of polymer chains in the condensed state has been intensively studied for several decades both experimentally and theoretically. These studies have demonstrated that the properties of polymers concerning molecular mobility are very unusual and complicated. The problem is well reviewed in a number of papers (e.g., ref 1 and 2). The major factor governing the overall molecular motion of a polymer chain in a dense system is the effect of entanglements caused by mutual uncrossability of neighboring polymer chains.

The recent picture of diffusion in entangled polymer systems is dominated by the idea of reptation. In the reptation model originally developed by de Gennes,[3] the polymer chains move along their own contours among their neighbors like a snake would move through a set of fixed obstacles. Lateral motions are strongly impeded by the neighboring chains, which make a tubelike region surrounding the chain contour.[4,5] To escape from the tube the chain has to diffuse along its entire contour length.

Predictions of the reptation model have evoked much recent experimental work on polymer diffusion in the melt (reviewed in ref 2). Results obtained with various experimental techniques have confirmed that the translational diffusion coefficient of N-mer chains varies as $D \approx N^{-2}$ in agreement with the reptation prediction for linear chains.

The reptation model is less successful, however, in describing the motion of branched or ring molecules where other mechanisms of relaxation and diffusion are necessary to understand the dynamics of these systems.[6] The weakness of chain-motion pictures based on the reptation model is that the chain is essentially considered as taking place between fixed obstacles. An infinitesimally small renewal of chain shape can eventually occur when the neighboring chains reptate away as considered, for example, by Klein.[7] This process is, however, noncomparably slower than the reptation itself. As a consequence, mobility of branched or ring molecules will be considerably frozen, which is not in agreement with experimental observations.[6]

Polymer chain motions have also been studied by computer simulations. The reptation mechanism[12] or various "relaxation" processes consisting in movement of one or few segments inside the chain[8-11] have been used to move chains on a lattice. Reptation and all known relaxation mechanisms can, however, only operate successfully when there are lattice sites still not occupied into which the relaxing structural units can move. They are therefore nonapplicable to models in which space is completely filled with chains.

In this paper a model of molecular motion in condensed macromolecular systems is suggested, which is based on the cooperative movement of an assembly of molecular subsegments belonging to various neighboring chains. The essential idea of the model is illustrated in Figure 1, where three chains taking part in the cooperative movement are shown. The movement consists of two contributing mechanisms: the first is based on position exchange between chain elements belonging to two different chains being locally in immediate contact (areas marked in the figure by circles) and the second consists in translational movement of chain subsegments along the chain contour between subsequent position-exchanging areas. The first type of movement involves local shape changes in both chains taking part in a position exchange. This demands, however, special local configurational arrangements of adjacent chains. The example shown in Figure 1 assumes that there is a kink on one of chains which can be pulled in and replaced by a kink formed on the other chain (Figure 1b). The second type of movement is equivalent to local chain reptation. It is assumed that all moving elements constitute a closed loop and can be regarded as a cooperatively moving assembly. Within the moving loops, chains move along their chain contours and the motion is transferred from one chain to another by position-exchanging units. The directions of respective motions are marked in Figure 1 by arrows. As a result of this motion, each element in the loop shifts to a new position occupied before by another adjacent element also belonging to the loop. This means that the motion is performed by collective replacements within the loop and no additional volume is needed for such a rearrangement. It has been noticed during the preparation of this manuscript

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