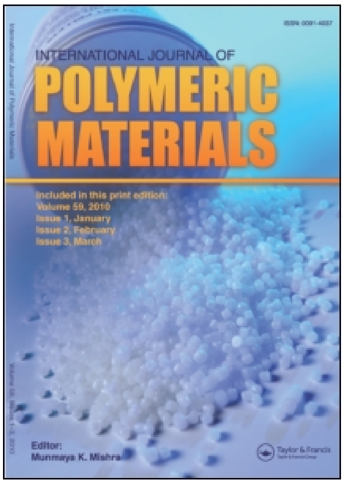

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Association of Stereoregular Poly(methyl methacrylates)†

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Isotactic and syndiotactic poly(methyl methacrylate) (*i*- and *s*-PMMA) form stereocomplexes in suitable solvents. Viscometric and turbidimetric studies of this stereoassociation have led us to divide the solvents into 3 types. Type A solvents are polar solvents which promote stereoassociation, resulting in gelation and precipitation. Type B solvents are nonpolar aromatic solvents, wherein stereoassociation is weaker but still leads to gelation. Type C solvents are very good solvents in which stereoassociation does not occur.

It appears that the so-called stereospecific replica polymerization of methyl methacrylate on stereoregular PMMA as a polymer matrix in the different types of solvents is closely related to the above mentioned tendency of *i*- and *s*-PMMA to associate. The replica efficiency of the matrix decreases in the order A > B > C = 0. The stereocomplexes formed *in situ* during stereospecific replica polymerization were investigated and compared with those obtained by mixing solutions of *i*- and *s*-PMMA. It seems that the 1:2 *i*/*s* stereocomplex which shows thermal properties quite different from its components, is the most stable one.

1 INTRODUCTION

In previous papers[1–4] we found that radical polymerization of methyl methacrylate (MMA) in the presence of stereoregular poly(methyl methacrylate) (PMMA) proceeds according to a stereospecific replica type mechanism in suitable solvents. The polymerization was syndiospecific in the presence of *i*-PMMA as a polymer matrix and isospecific in the presence of *s*-PMMA as a polymer matrix. The ability of *i*- and *s*-PMMA to promote stereospecific polymerization seems closely related to the tendency of *i*- and *s*-PMMA to associate under the prevailing conditions. This association was investigated by several authors[5–13] and was attributed to the formation of

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local associates of isotactic and syndiotactic chain segments. These associates were called stereocomplexes and were suggested to possess definite stoichiometric *iso–syndio* ratios like 1:2, 1:1, or 2:1.

In this paper we present further evidence for the close relationship between stereospecific replica polymerization and the formation of stereocomplexes in different solvents. Moreover, we try to elucidate the nature of the stereocomplexes by comparing some properties of complexes isolated from replica polymerizates with those obtained by mixing the *i*- and *s*-PMMA solutions.

2 EXPERIMENTAL

The techniques for synthesis of *i*- and *s*-PMMA for replica polymerization and isolation of *in situ* formed stereocomplexes, and for stereochemical characterization of polymerization products were described in preceding papers.[1–4] Data for the stereoregular PMMA's applied as polymer matrices in replica polymerization and used for the study of the association between *i*- and *s*- PMMA are compiled in Table I.

TABLE I

PMMA's used as matrices in replica polymerization and for stereocomplexation by mixing their solutions

		Triad content		
PMMA	$M_v \times 10^{-5}$	*i*	*h*	*s*
*i*MA1	5.3	0.94	0.03	0.03
*i*MA2	5.0	0.87	0.04	0.09
*i*MA3	7.6	0.92	0.06	0.02
*i*MA4	5.7	0.91	0.06	0.03
*i*MA5	7.5	0.94	0.03	0.03
*i*MA6	6.0	0.88	0.05	0.07
*i*MA7	3.0	0.90	0.04	0.06
*s*MA1	4.9	0.04	0.07	0.89
*s*MA2	3.5	0.05	0.09	0.86
*s*MA3	4.5	0.06	0.08	0.86
*s*MA4	4.5	0.02	0.07	0.91

The interaction between *i*- and *s*-PMMA was investigated by measuring reduced viscosities of various mixtures as functions of solvent type, temperature, concentration and time. The turbidities of mixed solutions were also estimated by measuring the decrease in light transmission at 450 nm in a VIS Jouan spectrophotometer. The thermal properties of the mixtures and the stereocomplexes of *i*- and *s*-PMMA were studied by a differential scanning calorimeter (DSC-1B Perkin-Elmer).

3 RESULTS AND DISCUSSION

3.1 Viscometry of mixed solutions

In Figure 1 the reduced viscosities (η_{sp}/c) are plotted against the fractional *s*-PMMA content (X_S) for different mixtures of 0.2% w/v solutions of *i*-PMMA and *s*-PMMA in various solvents at 25°C. The viscosities were measured 10 minutes after mixing the separate solutions.

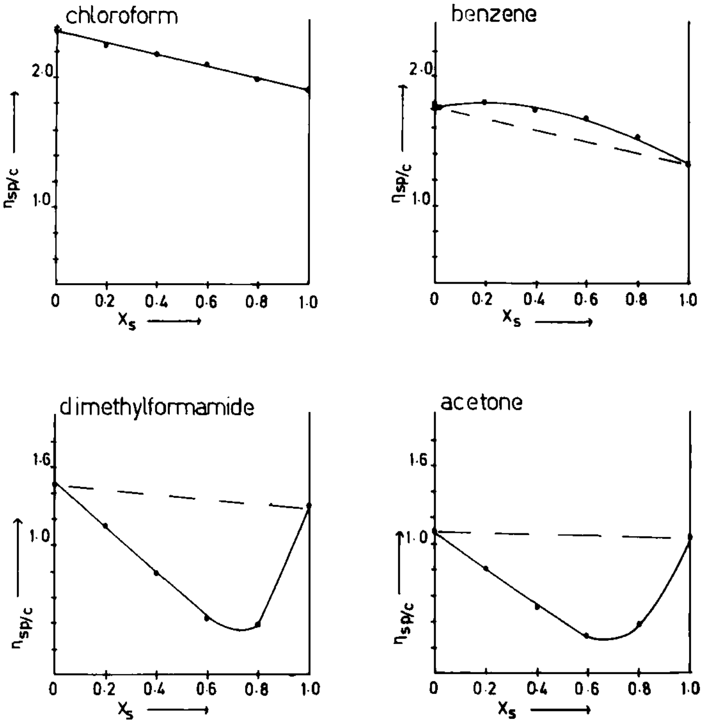

FIGURE 1 Reduced viscosity η_{sp}/c *vs.* *s*-PMMA content X_s for mixtures of *i*MA1 and *s*MA1 in various solvents measured 10 minutes after mixing the separate solutions at 25°C. The total polymer concentration is 0.2 g/dl.

In the polar solvents dimethylformamide (DMF) and acetone a minimum is obtained for $X_S = 0.67$, *i.e.*, at an *iso–syndio* ratio of 1:2. After some time these solutions become turbid due to precipitation of stereocomplexes (see Turbidimetry). These results do not agree with those of Liu *et al.*[6] concerning the reduced viscosity of acetone solutions of mixtures of *i*- and *s*-PMMA. Such polar solvents which are considered strongly complexing, are called type A solvents. Besides DMF and acetone, solvents like acetonitrile, dimethylsulphoxide, methyl isobutyrate, tetrahydrofuran and MMA monomer belong to type A.

In the nonpolar aromatic solvents benzene and toluene the deviations from additive behavior show a broad maximum around $X_s = 0.5$. However, this maximum is not stable in toluene and flattens as a function of time due to the formation of nearly invisible and strongly swollen gel particles. Toluene and benzene are considered weakly complexing, and designated type B solvents. Besides toluene and benzene, also the solvent thiophene belongs to this type.

Finally, in chloroform η_{sp}/c yields a nearly additive curve pointing to the absence of any association under these conditions. Hence, chloroform is called a non-complexing or type C solvent. The solvent dichloromethane belongs to the same type, which prevents stereoassociation because of too high a solvating power for both stereoregular PMMA's.

Since stereocomplexes dissociate at some elevated temperature the deviations from additivity in type A and B solvents decrease with increasing temperature. For DMF the deviation from additivity vanishes at 100°C, and for toluene at 90°C.[6] It is likely that these dissociation temperatures are dependent on the molecular weight of the used PMMA's. We found that the stereocomplex of samples *i*MA-1 and *s*MA-1 in benzene still exists at the normal boiling point whereas Rehage *et al.*[11] using *i*- and *s*-PMMA with molecular weights of 2.3×10^5 and 7×10^4, respectively, found a dissociation temperature in benzene of 65°C.

At higher concentrations ($\geqslant 0.5$ g/dl) there is a tendency of the viscometric curves to transform to those characteristic of type B solvents, *i.e.*, the minimum changes gradually into a maximum. Such a behavior may be explained by polymer chains having a greater chance to associate with several complementary chains, resulting in a larger number of smaller regions of associated chain segments which act as physical crosslinks and accordingly raise the viscosity. This situation corresponds with that in type B solvents at lower concentrations where the regions of association are also small, due to the weakly complexing properties of such solvents.

3.2 Turbidimetry

Turbidimetry can only be applied in the case of the strongly complexing type A solvents. In the weakly complexing type B solvents highly swollen gel particles are formed which do hardly diminish light transmission, whereas in the non-complexing type C solvents turbidity does not arise at all.

In type A solvents like DMF and acetone, the precipitation of stereocomplexes takes some time. Therefore, it appeared necessary to replace the normal technique of continuous turbidimetric titration of *i*-PMMA solution with *s*-PMMA solution by turbidimetric measurements of various premixed solutions as a function of time. The total polymer concentration was 0.2 g/dl and the temperature was about 20°C. Figure 2 shows the turbidities for mixtures of *i*- and *s*-PMMA in acetone as functions of X_S for several times. It is evident that a maximum arises again at $X_S = 0.67$, *i.e.*, at an *iso–syndio* ratio of 1:2.

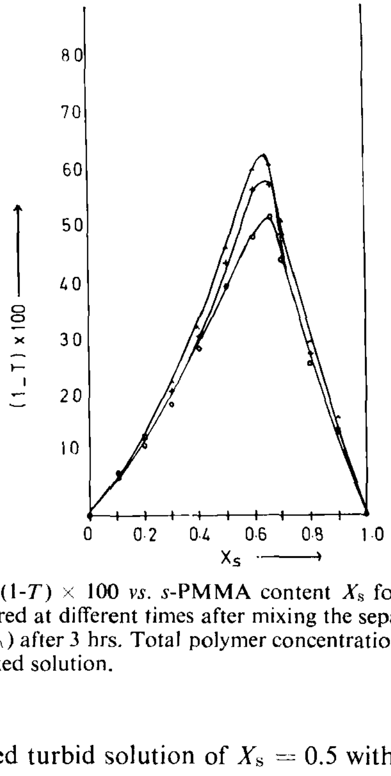

FIGURE 2 Turbidity (1-*T*) × 100 *vs*. *s*-PMMA content X_S for mixtures of *i*MA1 and *s*MA1 in acetone measured at different times after mixing the separate solutions: (○) after 1 hr., (+) after 2 hrs., (△) after 3 hrs. Total polymer concentration is 0.2 g/dl; *T* = the light transmittancy of the mixed solution.

By titrating an aged turbid solution of $X_S = 0.5$ with a *s*-PMMA solution the turbidity rises instantaneously and at $X_S = 0.67$ a final turbidity value is obtained which nearly equals that of Figure 2. However, when a turbid solution of $X_S = 0.67$ is titrated with *i*- or *s*-PMMA solution the turbidity decreases. When one corrects the original turbidity at $X_S = 0.67$ for dilution by the added *i*- or *s*-PMMA solution the turbidity remains practically constant. This means that the precipitated stereocomplex with *iso–syndio* ratio 1:2 is stable with respect to extra *i*- or *s*-PMMA. From NMR measurements we know that the precipitates at $X_S = 0.5$ and 0.67 had microstructures corresponding to *i*/*s* ratio of 1:1 and 1:2, respectively. So, we may conclude from the turbidimetric results that the solubility of the stereocomplex at *i*/*s* ratio of 1 : 1 in acetone is much higher than that of the stereocomplex at *i*/*s* ratio of 1 : 2. In future experiments we shall measure the solubility as well as the microstructure of the precipitates produced at various values of X_s.

3.3 Replica polymerization

In the context of this paper we confine ourselves to those results which accentuate the relationship between stereospecific replica polymerization and the tendency of *i*- and *s*-PMMA to form a stereocomplex.

The influence of the polymer matrix on the kinetics of replica polymerization is demonstrated by Figure 3, wherein the average molecular weight of the formed polymer is plotted versus the average molecular weight of the polymer matrix for polymerizations in DMF at 25°C. From this figure it may be deduced that the replication effect weakens in the order *i*-PMMA > *s*-PMMA > *c*-PMMA (= blank polymerization = 0). This can be explained by the normal tendency of MMA to add syndiotactically, so that *i*-PMMA matrix promotes this tendency whereas *s*-PMMA matrix has to oppose it.

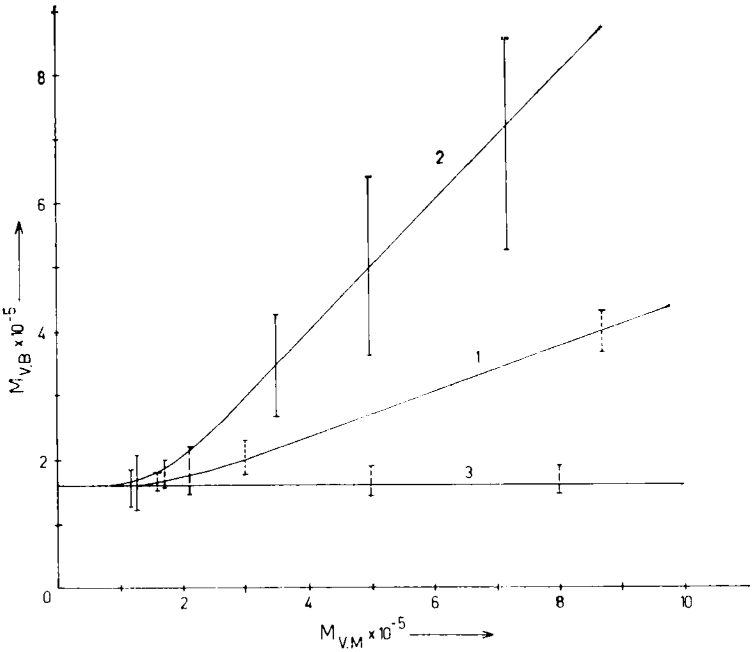

FIGURE 3 The molecular weight of the total polymer formed ($M_{V,B}$) *vs.* the molecular weight of the polymer matrix ($M_{V,M}$) for polymerizations in the presence of (1) preformed *s*-PMMA, (2) preformed *i*-PMMA, and (3) preformed *c*-PMMA. Reprinted from Ref. (2) by courtesy of John Wiley & Sons, Inc.

The effect of temperature on the replica polymerization was investigated in detail in the type A solvent DMF between 0 and 100°C.[3] The syndiospecificity of the polymerization in the presence of *i*-PMMA matrix vanished at about 100°C, which agrees with the complete dissociation of the stereocomplexes at this temperature.

The best proof of the relationship between stereospecific replica polymerization and stereocomplex formation is produced by the effect of solvent type on both phenomena. In Figure 4 the microstructure of the polymer formed and complexed with the *i*-PMMA matrix in the insoluble fraction of the polymerizate is plotted against MMA conversion for replica polymerizations in the type A solvents DMF, acetonitrile, and acetone. In Figure 5 the same is plotted for replica polymerizations in the type B solvent toluene. It is evident that in this case the syndiotacticity of the formed polymer is lower than in the type A solvents. In a type C solvent like chloroform no insoluble fraction arises at all, and the microstructures of the total polymer formed in the presence or absence of *i*-PMMA matrix are about equal to that of conventional PMMA:

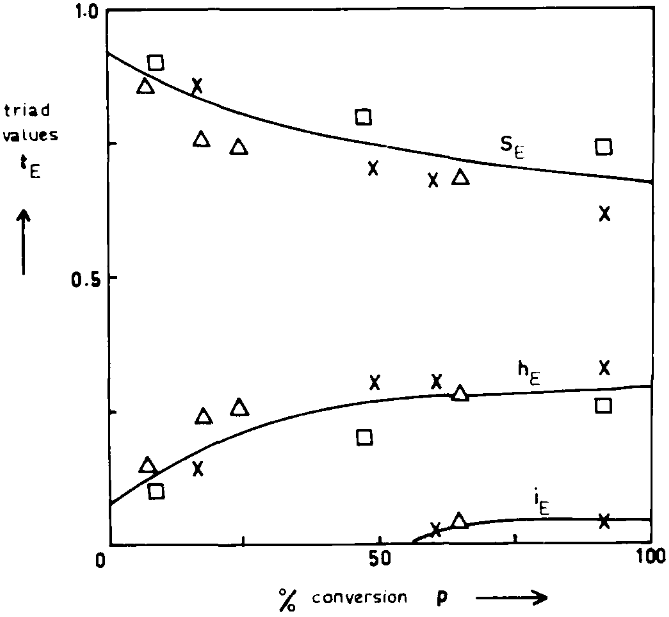

FIGURE 4 Triad contents t_E of polymers formed in the presence of *i*-PMMA matrices (*i*MA2 and *i*MA3) and complexed in the insoluble fraction *vs.* conversion *p* in DMF (□), acetonitril (×), and acetone (△). Data by R. Buter, Y. Y. Tan, and G. Challa, *J. Polymer Sci., Polym. Chem. Ed.* **11**, 2977 (1973). Reprinted by courtesy of John Wiley & Sons, Inc.

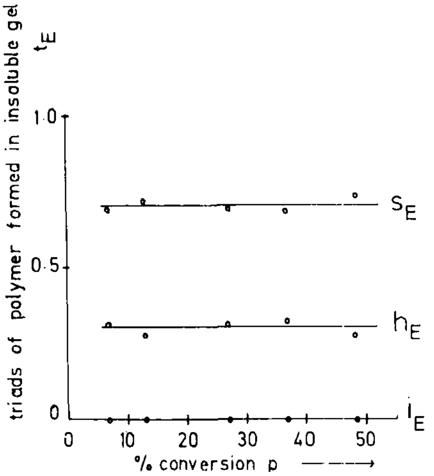

FIGURE 5 Microstructure of polymers formed and complexed in the insoluble gel fractions obtained from polymerizations of MMA in the presence of preformed *i*MA1 in toluene at 25°C.

$i = 0.07$, $h = 0.25$, $s = 0.68$. Comparing the results of replica polymerization on *s*-PMMA as a polymer matrix we get the following overall picture: (1) In type A solvents the isospecificity is high at low conversions ($i \approx 0.85$, $h \approx 0.15$, $s = 0$ for the formed polymer complexed in the insoluble fraction); (2) In type B solvents nearly conventional microstructures are formed, which demonstrates that the stereocomplexation is too weak to oppose the normal tendency of MMA to add more syndiotactically; (3) In type C solvents the effect of this matrix is zero as it was for the *i*-PMMA matrix.

Summarizing, we conclude that the replica efficiency in different solvents decreases in the order type A > type B > type C = 0, which is the same order as found before with respect to the strength of the stereocomplexation of *i*- and *s*-PMMA.

3.4 The nature of stereocomplexes

Although *i*- and *s*-PMMA produce complexes in every ratio we think that the 1:2 *i*/*s* stereocomplex is the most stable one and that deviations from this stoichiometric ratio are due to uncomplexed chain segments between the local clusters of complexed chain segments. Therefore we preferred to study the complexes which precipitated from dilute mixed solutions of 1:2 *i*- and *s*-PMMA in type A solvents and the complexes formed *in situ* during replica polymerization in the same solvents with *i*- or *s*-PMMA as polymer matrix. In order to attain the desired *i*/*s* ratio of 1:2, the precipitated complexes were isolated at high monomer conversions for *i*-PMMA matrix and at low conversions for *s*-PMMA matrix. After drying the samples we measured their thermal properties on a differential scanning calorimeter DSC-1B Perkin-Elmer). The results are compiled in Table II and compared with those of *i*- and *s*-PMMA.

TABLE II

Thermal data of PMMA's and 1 : 2 *i*/*s* stereocomplexes

Material	T_g(°C)	T_m(°C)	Remarks
i-PMMA (*i*MA4)	38	165	Melting point obtained after annealing at 140°C for a few days
s-PMMA (*s*MA2)	120	(255)	Melting accompanied by degradation
Stereocomplex from mixed *i*MA5 and *s*MA3 solutions in THF	88	179 and 210	The T_g jump is very small and may be due to uncomplexed mixture of *i*- and *s*-PMMA
Stereocomplex from mixed *i*MA6 and *s*MA4 solutions in acetone	none observed	213	By annealing the melting point can be raised up to 234°C
Stereocomplex from replica polymerization with *i*MA5 as polymer matrix in THF	none observed	197	In the second scan a small T_g jump observed at about 100°C
Stereocomplex from replica polymerization with *i*MA7 as polymer matrix in acetone	none observed	189	,, ,, ,,
Stereocomplex from replica polymerization with *s*MA4 as polymer matrix in THF	none observed	223	,, ,, ,,
Stereocomplex from replica polymerization with *s*MA4 as polymer matrix in acetone	none observed	212, 237	The melting peak is very broad

From Table II it is obvious that more complete stereocomplexes can be obtained by replica polymerization though the total polymer concentration (up to 24% w/v) is much higher than in the mixed solution. This can be understood by the replica mechanism which forces the growing chain to follow the contour of the complementary matrix chain. For this reason we believe that the structure of Liquori[9] for the 1: 2 *i*/*s* complex with the *s*-chains tilted by about 60° with respect to the helical axis of the *i*-chains is not correct for the stereocomplexes obtained by replica polymerization, for which one should expect the growing chain to be more or less parallel to the matrix chain.

Acknowledgement

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DISCUSSION

Prof. H.-G. Elias (*Midland Macromolecular Institute, Midland, Michigan*): According to your data, a certain minimum molecular weight of the matrix is needed for an effect of the stereocontrol of the polymerization. Do you think that this is due to an increased probability of occurrence of longer stereoregular sequences in the case of higher molecular weights?

Prof. G. Challa: Yes, I think so, but in addition to this, longer matrix chains will also produce more stable stereocomplexes. So, their dissociation during replica polymerization will be suppressed to a greater extent, and this improves the stereocontrol.

Prof. H.-G. Elias: I agree with your explanation because the free radical polymerization of *p*(*tert*-butyl)-vinylbenzoate leads to crystallinity in the case of high molecular weights but not in the case of low molecular weights. The effect was explained by the higher probability of longer stereoregular sequences in the high molecular weight materials [M. A. Osman and H.-G. Elias, *J. Macromol. Sci. A* **5,** 805 (1971)].

Prof. S. Krause (*Renssealer Polytechnic Institute, Troy, New York*): If methyl methacrylate monomer is a type A solvent, one would expect ordinary free-radical initiated bulk polymerization of methyl methacrylate to proceed as follows: first, some conventional, about 70% syndiotactic polymer molecules should form, and then these should cause formation of some predominantly isotactic molecules. Is there any evidence for the presence of predominantly isotactic polymer molecules in samples of bulk polymerized poly(methyl methacrylate)?

Prof. G. Challa: There is no evidence for the presence of such polymer molecules. However, from abnormal solution properties of conventional PMMA it has been concluded that some intermolecular association takes place between short isotactic and syndiotactic segments. In fact, the stereoregular sequences are too short for yielding complexes which are stable enough to promote stereospecific replica polymerization. On the other hand, we could obtain such polymerization in bulk systems without radical initiator by using higher reaction temperature and some tactic poly(methyl methacrylate) as matrix.

Dr. M. Shinohara (*Dow Corning, Midland, Michigan*): Is such replica polymerization applicable to other than methyl methacrylate—poly(methyl methacrylate) systems?

Prof. G. Challa: Yes, we expect so. In fact, we are trying to prove that for a few related systems.

Dr. M. Shinohara: What is the driving force for adsorption of methyl methacrylate monomer onto stereoregular poly(methyl methacrylate) in such polar solvents as dimethylformamide, dimethylsulfoxide or acetone?

Prof. G. Challa: We do not think that methyl methacrylate is preferentially adsorbed in these solvent systems. Only the growing poly(methyl methacrylate) chain is adsorbed after it has attained a certain minimal length.

Dr. M. Shinohara: Have you investigated the kinetics of replica polymerization in the system methyl methacrylate — poly(methyl methacrylate)? Does the presence of pre-polymer alter the rate of methyl methacrylate consumption?

Prof. G. Challa: Some preliminary results of such investigation were given in the figure showing the relationship between molecular weights of matrix polymer and formed polymer. Further results not presented here, indicate an alteration of rate as compared to blank polymerization. We expect that in addition to the normal Trommsdorff effect, a so-called complex-effect will also be found.