# Miscibility of Poly(methoxymethyl Methacrylate) and Poly(methylthiomethyl Methacrylate) with Poly(styrene-co-Acrylonitrile) and Poly(*p*-Methylstyrene-co-Acrylonitrile)

S. H. GOH,* S. Y. LEE, and C. L. LEONG

Department of Chemistry, National University of Singapore, Singapore 0511, Republic of Singapore

**SYNOPSIS**

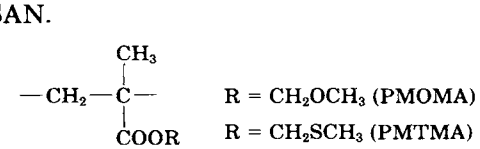
The miscibility of poly(methoxymethyl methacrylate) (PMOMA) and poly(methylthiomethyl methacrylate) (PMTMA) with poly(styrene-co-acrylonitrile) (SAN) and poly(*p*-methylstyrene-co-acrylonitrile) (*p*MSAN) was studied by differential scanning calorimetry. PMOMA is miscible with SAN having an acrylonitrile (AN) content around 30 wt %. However, PMOMA is immiscible with any of the *p*MSAN samples. PMTMA is miscible with SAN having AN contents between 9 and 36 wt % and with *p*MSAN having AN contents between 19 and 34 wt %. The miscibility of the blends enables the evaluation of various segmental interaction parameters.

## INTRODUCTION

Polymers are generally immiscible with each other unless there are specific interactions between them.[1] However, in the absence of specific interaction a homopolymer may be miscible with a copolymer over a certain copolymer composition range, exhibiting a "miscibility window." The intramolecular interaction between two different types of segments in the copolymer plays an important role in determining the miscibility behavior of a homopolymer/copolymer blend.[2-4] Blends of poly(methyl methacrylate) (PMMA),[5-7] poly(ethyl methacrylate) (PEMA),[5] and poly(*n*-propyl methacrylate) (P*n*PMA)[5] with poly(styrene-co-acrylonitrile) (SAN) exhibit such miscibility windows.

The miscibility behavior of poly(alkyl methacrylate)s with poly(α-methylstyrene-co-acrylonitrile) (α*MSAN*) and poly(*p*-methylstyrene-co-acrylonitrile) (*p*MSAN) has also been reported. PMMA[8,9] and PEMA[8] are miscible with an α*MSAN* sample containing 30 wt % acrylonitrile (AN). Our recent study also shows that blends of PMMA, PEMA, and P*n*PMA with *p*MSAN also exhibit miscibility windows.[10]

In a recent series of studies, we examined the miscibility behavior of polymethacrylates that contain other functional moieties in their pendant ester groups. These polymethacrylates including poly(chloromethyl methacrylate) (PCMMA) and poly(tetrahydrofurfuryl methacrylate) (PTHFMA) are miscible with SAN[11,12] and with an α*MSAN* sample containing 30 wt % AN.[12,13] We have also examined the miscibility of poly(methoxymethyl methacrylate) (PMOMA) and poly(methylthiomethyl methacrylate) (PMTMA). Both PMOMA and PMTMA are miscible with α*MSAN* (30 wt % AN).[13,14] However, PMOMA, but not PMTMA, is miscible with PMMA and poly(vinylidene fluoride) (PVDF).[15,16] In this communication, we report the miscibility of PMOMA and PMTMA with SAN and *p*MSAN.




## EXPERIMENTAL

### Materials

Methoxymethyl methacrylate and methylthiomethyl methacrylate were prepared following the procedures

* To whom correspondence should be addressed.

Journal of Applied Polymer Science, Vol. 44, 199–204 (1992)
 CCC 0021-8995/92/020199-06$04.00

reported by Ueda and coworkers.[17,18] PMOMA and PMTMA were prepared by solution polymerization as described elsewhere.[15] The number-average molecular weight ($M_n$) of PMOMA is 17,000 and the weight-average molecular weight ($M_w$) of PMTMA is 48,000 from intrinsic viscosity measurements using the appropriate Mark–Houwink equations.[17,18]

An SAN sample containing 22 wt % AN was obtained from Monsanto. Two other SAN samples with AN contents of 25 and 30 wt % were obtained from Scientific Polymer Products, Inc. Other SAN and *p*MSAN samples were prepared by solution polymerization in 2-butanone at reflux temperature for 4 h using 0.30 wt % azobisisobutyronitrile as initiator. The AN contents of the copolymers were determined by elemental analysis for nitrogen. In the following discussion, the number after SAN or *p*MSAN denotes the weight percentage of AN in the copolymer. The characteristics of the copolymers are shown in Table I.

### Preparation of Blends

Various blends were prepared by solution casting from tetrahydrofuran. The solvent was allowed to evaporate slowly at room temperature. The blends were then dried *in vacuo* at 110°C for 3 d.

**Table I Characteristics of Copolymers**

| Sample | $M_n$ | $M_w$ | $T_g$ (°C) |
|---|---|---|---|
| SAN3.1 | 14,000 | 23,000 | 101 |
| SAN8.4 | 9,400 | 17,000 | 102 |
| SAN9.8 | 20,000 | 31,000 | 103 |
| SAN13.4 | 7,600 | 15,000 | 102 |
| SAN19.8 | 21,000 | 33,000 | 104 |
| SAN22.0 | 51,000 | 116,000 | 103 |
| SAN25.0 | 66,000 | 156,000 | 102 |
| SAN30.0 | 61,000 | 125,000 | 100 |
| SAN34.5 | 21,000 | 29,000 | 110 |
| SAN40.0 | 31,000 | 47,000 | 110 |
| *p*MSAN7.7 | 21,000 | 34,000 | 107 |
| *p*MSAN10.2 | 28,000 | 34,000 | 110 |
| *p*MSAN13.6 | 21,000 | 42,000 | 105 |
| *p*MSAN15.8 | 28,000 | 46,000 | 105 |
| *p*MSAN18.3 | 22,000 | 36,000 | 106 |
| *p*MSAN19.6 | 27,000 | 43,000 | 109 |
| *p*MSAN21.3 | 28,000 | 52,000 | 105 |
| *p*MSAN26.5 | 27,000 | 44,000 | 105 |
| *p*MSAN29.1 | 34,000 | 56,000 | 105 |
| *p*MSAN32.3 | 38,000 | 62,000 | 104 |
| *p*MSAN35.9 | 31,000 | 50,000 | 104 |

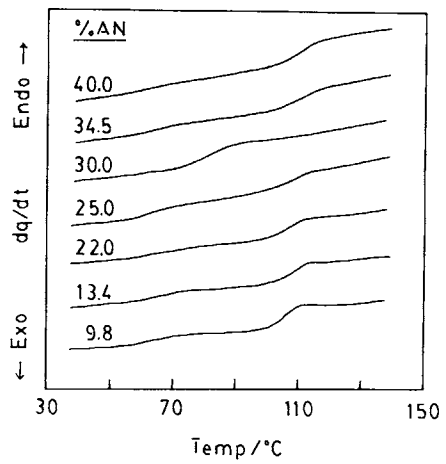



**Figure 1** DSC curves of various PMOMA/SAN (50/50) blends.

### Measurements of Glass Transition Temperature

The glass transition temperatures ($T_g$) of various samples were measured with a Perkin–Elmer DSC-4 differential scanning calorimeter using a heating rate of 20°C/min. The initial onset of the change of slope in the DSC curve was taken as $T_g$.

### Measurements of Cloud Point

The miscible blends were examined for the existence of lower critical solution temperature (LCST) behavior. The cloud points of the miscible blends were determined using the method described previously.[19]

## RESULTS AND DISCUSSION

### PMOMA/SAN Blends

Figure 1 shows the DSC curves of various PMOMA/SAN (50/50) blends. Except for the PMOMA/SAN30.0 blend, which shows only one glass transition, the blends show two glass transitions. The results show that PMOMA is miscible with SAN30.0 but not with the other SAN samples. The two $T_g$ values for an immiscible blend are close to those of PMOMA ($T_g$ = 56°C) and the respective SAN sample. The $T_g$–composition curve for the miscible PMOMA/SAN30.0 blends is shown in Figure 2.

All immiscible blends were cloudy. In contrast, PMOMA/SAN30.0 blends were transparent but turned cloudy upon heating, showing LCST behavior. The cloud point curve for PMOMA/SAN30.0 blends is shown in Figure 2. PMOMA/$\alpha$MSAN30

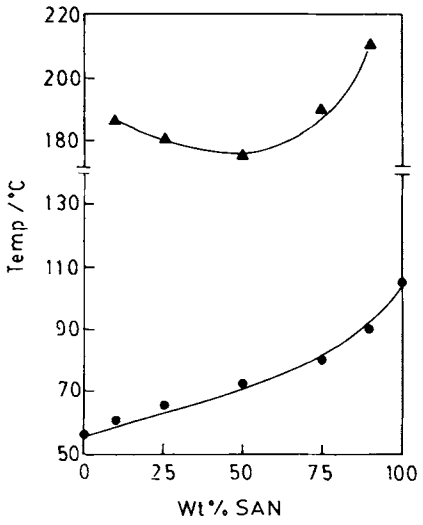



**Figure 2** (●) $T_g$–composition curve and (▲) cloud point curve of PMOMA/SAN30.0 blends.

blends also show LCST behavior.[13] The results show that PMOMA is miscible with SAN over a narrow copolymer composition range around 30 wt % AN.

## PMOMA/pMSAN Blends

Figure 3 shows the DSC curves of various PMOMA/*p*MSAN (50/50) blends. Two glass transitions were observed in each of the blends. The $T_g$ values are close to those of PMOMA and the respective *p*MSAN samples. Moreover, all the blends were cloudy. The results show that PMOMA is immiscible with any of the *p*MSAN samples.

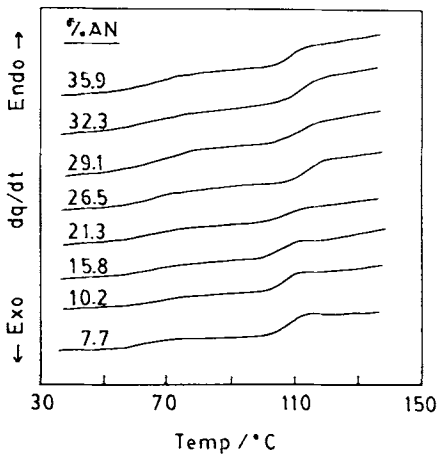



**Figure 3** DSC curves of various PMOMA/*p*MSAN (50/50) blends.

## PMTMA/SAN Blends

Figure 4 shows the DSC curves of various PMTMA/SAN (50/50) blends. PMTMA/SAN3.7 blends were cloudy and each showed two $T_g$s, indicating the two-phase nature of the blends. The lower $T_g$ value is about 10°C higher than that of PMTMA ($T_g$ = 53°C), indicating the presence of SAN3.7 in the pMTMA-rich phase, but the upper $T_g$ value is close to that of SAN3.7.

PMTMA/SAN8.4 blends were also cloudy and each blend showed two $T_g$s. Similar to the PMTMA/SAN3.7 blends, the lower $T_g$ is about 10°C higher than that of PMTMA. However, the upper $T_g$ is about 85°C, almost 20°C lower than that of SAN8.4. The results show that PMTMA is present in the SAN8.4-rich phase.

All blends of PMTMA with SAN9.8, SAN13.4, SAN19.8, SAN25.0, SAN30.0, and SAN34.5 were transparent, and each of the blends showed only one composition-dependent $T_g$. Therefore, PMTMA is miscible with these SAN samples. The $T_g$–composition curves of the six miscible blend systems are shown in Figure 5. Except for PMTMA/SAN34.5 blends, which showed LCST behavior, the miscible blends remained transparent upon heating to 280°C. The cloud point curve for PMTMA/SAN34.5 blends is shown in Figure 6. The existence of LCST behavior for PMTMA/SAN34.5 blends also suggests that SAN34.5 is near the edge of the miscibility window. Indeed, PMTMA/SAN40.0 blends were cloudy and each showed two $T_g$s close to those of PMTMA and SAN40.0. The results show that

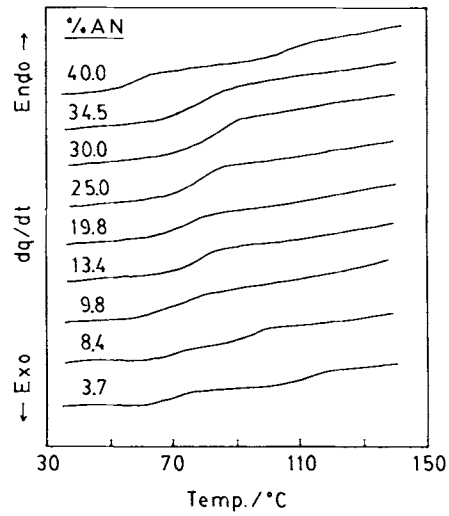



**Figure 4** DSC curves of various PMTMA/SAN (50/50) blends.

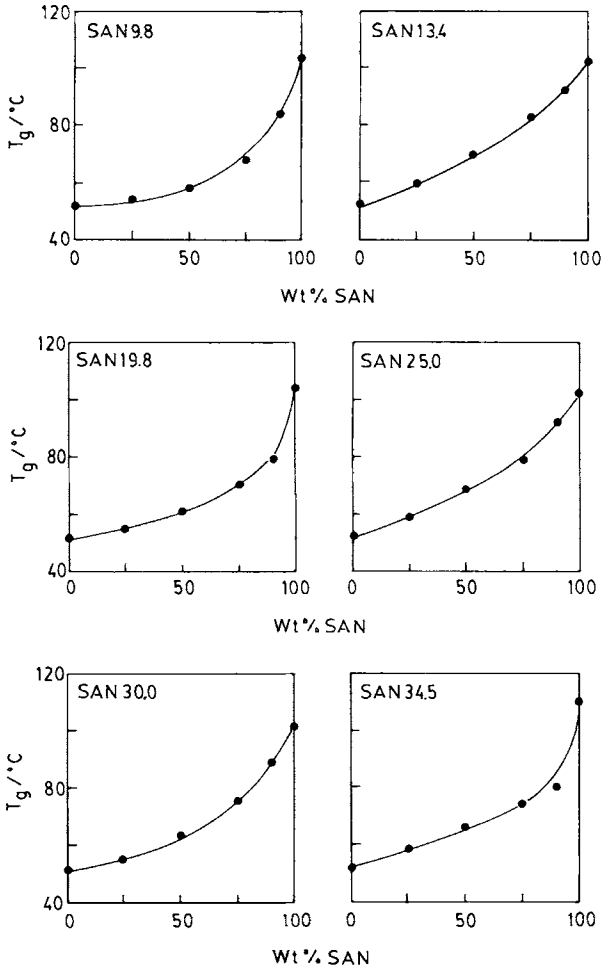



**Figure 5** $T_g$–composition curves of various miscible PMTMA/SAN blends.

PMTMA is miscible with SAN having AN contents between 9 and 36 wt %; the phase diagram is shown in Figure 7.

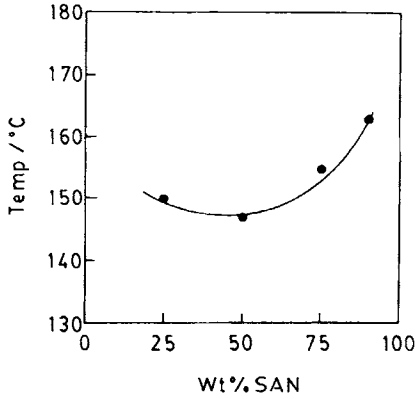



**Figure 6** Cloud point curve of PMTMA/SAN34.5 blends.

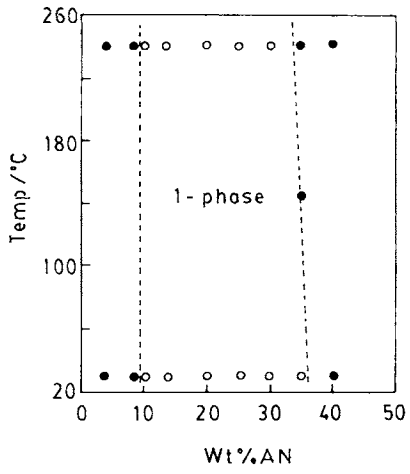



**Figure 7** Phase diagram of PMTMA/SAN blends. (○), miscible blend; (●), immiscible blend.

## PMTMA/*p*MSAN Blends

Blends of PMTMA with *p*MSAN10.2, *p*MSAN13.6, *p*MSAN18.3, and *p*MSAN35.9 were cloudy and each blend showed two $T_g$s, indicating that these blends were two-phase blends. The DSC curves of various 50/50 blends are shown in Figure 8. In general, the lower $T_g$ is close to that of PMTMA and the upper $T_g$ is about 10°C lower than that of the respective *p*MSAN.

Blends of PMTMA with *p*MSAN19.6, *p*MSAN26.5, *p*MSAN29.1, and *p*MSAN32.3 were transparent and remained so upon heating to 280°C. In addition, each of these blends showed one composition-dependent $T_g$; the $T_g$–composition curves of the four blend systems are shown in Figure 9. The

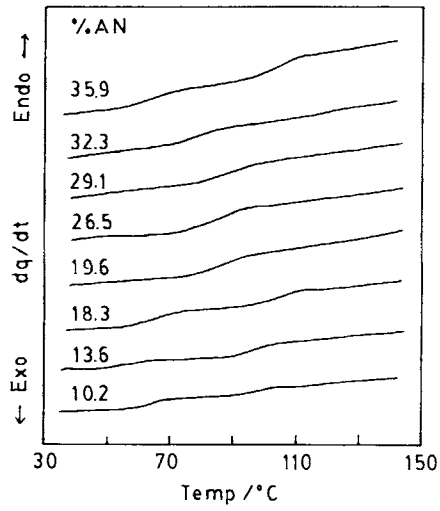



**Figure 8** DSC curves of various PMTMA/*p*MSAN (50/50) blends.

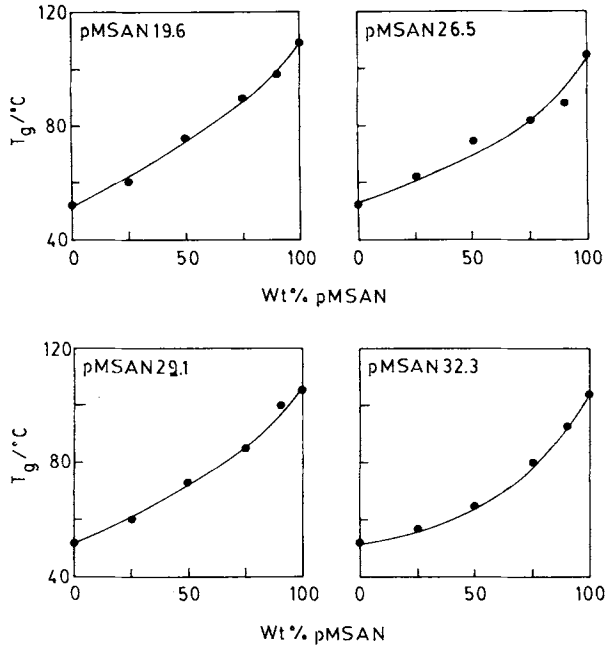



**Figure 9** $T_g$–composition curves of various PMTMA/*p*MSAN blends.

results show that PMTMA is miscible with *p*MSAN having AN contents between 19 and 34 wt %; the phase diagram is shown in Figure 10.

## Miscibility Behavior

The miscibility of a homopolymer A/copolymer BC blend system is often explained by a simple binary interaction model[2-4] that takes into consideration various segmental interactions. The net interaction parameter, $\chi_{blend}$, is expressed by the equation

$$\chi_{blend} = y\chi_{A/C} + (1-y)\chi_{A/B} - y(1-y)\chi_{B/C}, \quad (1)$$

where $y$ is the volume fraction of segment $C$ in the copolymer. For the formation of a miscible blend, $\chi_{blend}$ must be smaller than $\chi_{crit}$, which is related to the degrees of polymerization $N$ of the two polymers by the equation

$$\chi_{crit} = \tfrac{1}{2}[N_1^{-1/2} + N_2^{-1/2}]^2.$$

The value of $\chi_{crit}$ depends more on the polymer with a smaller $N$ value and it approaches zero when both $N_1$ and $N_2$ are sufficiently large. The miscibility of a homopolymer/copolymer blend system can be used to evaluate various segmental interaction parameters.[3,7,20-22] Conversely, a knowledge of various segmental interaction parameters enables the prediction of the phase behavior of the blend system.[23-25]

For PMOMA/SAN system, eq. (1) becomes

$$\chi_{blend} = y\chi_{MOMA/AN} + (1-y)\chi_{MOMA/S} - y(1-y)\chi_{S/AN},$$

where $y$ is the volume fraction of AN in SAN. If the $N$ values for PMOMA and SAN are taken to be 130 and 400, respectively, $\chi_{crit}$ is then 0.0095. The phase boundaries are considered to locate at 28 and 32 wt % AN, corresponding to $y$ values of 0.26 and 0.30. Based on these $y$ values, and a value of 0.829 for $\chi_{S/AN}$,[7] $\chi_{MOMA/S}$ and $\chi_{MOMA/AN}$ are found to be 0.074 and 0.44, respectively.

For PMOMA/*p*MSAN blend system, $\chi_{blend}$ is expressed by the equation

$$\chi_{blend} = y\chi_{MOMA/AN} + (1-y)\chi_{MOMA/pMS} - y(1-y)\chi_{pMS/AN}.$$

The value of $\chi_{pMS/AN}$ is 0.91,[26] which is larger than $\chi_{S/AN}$. The immiscibility of PMOMA with *p*MSAN then implies that $\chi_{MOMA/pMS}$ must be larger than $\chi_{MOMA/S}$ such that $\chi_{blend}$ is larger than $\chi_{crit}$ at all $y$ values. This implication is consistent with several recent reports that the segmental interaction parameter between *p*-methylstyrene and another segment is larger than that between styrene and the same reference segment.[26-29] The immiscibility of PMOMA/*p*MSAN blends can then be attributed to a strong repulsive intermolecular interaction be-

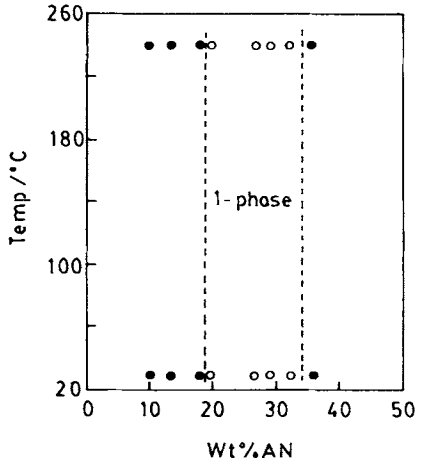



**Figure 10** Phase diagram of PMTMA/*p*MSAN blends. (○), miscible blend; (●), immiscible blend.

tween $p$-methylstyrene and methoxymethyl methacrylate segments.

Similarly, the segmental interaction parameters for the PMTMA blend systems can also be evaluated. In this case, $\chi_{pMS/AN}$ is 0.91 and the degree of polymerization of PMTMA is about 170. If the $N$ values for SAN and $p$MSAN are both taken to be 400, $\chi_{crit}$ is then 0.0068. For the PMTMA/SAN blend system, the boundaries are at 9 and 36 wt % AN, corresponding to $y$ values of 0.083 and 0.34. Application of eq. (1) leads to values of 0.031 and 0.51 for $\chi_{MTMA/S}$ and $\chi_{MTMA/AN}$, respectively. For the PMTMA/$p$MSAN system, the boundaries are at 19 and 34 wt % AN, corresponding to $y$ values of 0.18 and 0.32. $\chi_{MTMA/pMS}$ and $\chi_{MTMA/AN}$ are then found to be 0.059 and 0.51, respectively. The $\chi_{MTMA/AN}$ values evaluated from the two blend systems are identical. Furthermore, $\chi_{MTMA/pMS}$ is about twice of $\chi_{MTMA/S}$, indicating a stronger repulsive interaction between MTMA and $p$MS segments than that between MTMA and S segments. The indication is once again consistent with the above-mentioned general observation that there is a stronger repulsive interaction involving $p$MS segment as compared with S segment. Another interesting point is that the interaction parameter for methacrylate/styrene interaction becomes smaller and that for methacrylate/acrylonitrile interaction becomes larger when the ether oxygen in the MOMA segment is replaced by sulfur.

Nishimoto and coworkers[20] recently studied the miscibility of SAN with some methyl methacrylate-based copolymers. They found that the interactions of AN with styrene and methacrylate are strongly repulsive, whereas the interaction of styrene with the methacrylate is very weakly repulsive. The magnitudes of the $\chi$ values obtained from the present study are consistent with their findings.

The authors thank the National University of Singapore for its financial support of this research and Miss C. S. Lee for determining the molecular weights of SAN and $p$MSAN samples.

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*Received December 18, 1990*
*Accepted January 30, 1991*