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Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

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Anatoly Kim^a; Hyung-Joong Kim^b; Eun-Mi Lee^b; Jae-Rock Lee^b

^a Department of Chemistry, Tashkent State University, Tashkent, Vuzgorodok, Uzbekistan CIS ^b Korea Research Institute of Chemical Technology, Taejon, Korea

To cite this Article Kim, Anatoly , Kim, Hyung-Joong , Lee, Eun-Mi and Lee, Jae-Rock(1996) 'Some Peculiarities of the Radical Polymerization of Methyl Methacrylate in the Presence of Low Molecular Weight Liquid Crystals', Journal of Macromolecular Science, Part A, 33: 11, 1621 – 1631

To link to this Article: DOI: 10.1080/10601329608010927

URL: <http://dx.doi.org/10.1080/10601329608010927>

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SOME PECULIARITIES OF THE RADICAL POLYMERIZATION OF METHYL METHACRYLATE IN THE PRESENCE OF LOW MOLECULAR WEIGHT LIQUID CRYSTALS

ANATOLY KIM

Department of Chemistry
Tashkent State University
Tashkent 700095, Vuzgorodok, Uzbekistan, CIS

HYUNG-JOONG KIM,* EUN-MI LEE, and JAE-ROCK LEE

Korea Research Institute of Chemical Technology
Taejon, Korea 305-606

Key Words: Radical polymerization; Methyl methacrylate; Liquid crystal; Chain transfer reaction

ABSTRACT

Radical polymerization of methyl methacrylate (MMA) in the presence of propylbenzene, benzonitrile, their equimolar mixture, and a mixture of nematic liquid crystals (LC) was studied. Chain transfer reaction and unexpected dependence of the initial polymerization rate on LC concentration were revealed by means of UV spectrophotometry, viscometry, and dilatometry. The chain transfer reaction which occurred at the boundary of LC domains in the polymer matrix caused binding of some of the LC molecules to the macromolecules of PMMA. An increase in the initial rate of polymerization and a decrease of polydispersity were explained with formation of the LC phase because growth of the macroradicals continued not only in the homogeneous polymer phase but simultaneously also at the interfacial boundary between the polymer *matrix* and the LC phase. It is assumed that the LC molecules anchored

to the PMMA matrix can affect the mobility of free LC molecules in the LC domains when an external electric field is applied to LC/polymer composite films.

INTRODUCTION

Over the last ten years many scientists have been interested in fabrication and characterization of 10–20 μm thick polymer/liquid crystal (LC) composite films, so-called polymer dispersed liquid crystal (PDLC) films, which consist of a polymer matrix (or binder) and micron sized LC droplets dispersed in the polymer matrix [1]. In the PDLC film the LC molecules are oriented to the electric field direction when an external electric field is loaded. This property of a LC leads to optical anisotropy and matching/mismatching of refractive indices between the polymer matrix and a LC under an electrical on-off condition. Currently PDLC films are under investigation for utilization as light switchable windows, large reflective displays, LC projection displays, etc.

It is known that the electrooptical properties of PDLC systems depend on the size and shape of dispersed LC droplets (domain) which can be formed during polymerization due to phase separation from the initially homogeneous system [2]. The formation of an LC phase which takes place during polymerization may lead to altering the rate of polymerization. Only a small amount of work on the polymerization of different methacrylates in liquid crystalline solvents has been reported [3–6]. Most of them expected that ordered solvents would yield polymers having better stereoregularity. However, Deshpande and Aravindakshan [3] concluded that the tacticity of the resulting polymers was little influenced by LC materials in a radical polymerization system. On the other hand, in their work the possibility of a chain transfer reaction, which may occur during radical polymerization in the presence of LC solvents, between the LC molecules and the polymer radicals was not considered.

In this work we reveal some peculiar results, especially the possibility of a chain transfer reaction, which are found in the radical polymerization of methyl methacrylate (MMA) in a LC medium.

EXPERIMENTAL

Materials

A nematic type of low molecular weight LC mixture, E-7 (Merck Co., GB), which is composed of 4'-pentyl-4-biphenyl carbonitrile, 4'-heptyl-4-biphenyl carbonitrile, 4'-octyl-4-biphenyl carbonitrile, and 4'-pentyl-4-triphenyl carbonitrile, was used as the LC material. Methyl methacrylate (MMA, Junsei Chem. Co., Japan) was purified by removing the inhibitor with aqueous alkali solution and distillation under reduced pressure (46°C/100 mmHg, n_D^{20} 1.4140). Azobisisobutyronitrile (AIBN, Junsei Chem. Co., Japan) as a radical initiator was recrystallized from acetone and dried under vacuum (dec. 107°C). For the polymerization solvents, chloroform, benzene, benzonitrile, and propylbenzene were carefully purified and dried by conventional methods [7].

Polymerization Procedure

Solution polymerization of MMA in various solvents was carried out in a glass dilatometer (in the case of high conversion, a special glass dilatometer was used). Prepared mixtures consisting of monomer, LC, initiator, and solvent were placed in the dilatometer, then degassed and sealed under vacuum. The dilatometer was immersed in a water bath at $60 \pm 1^\circ\text{C}$. Conversion (%) from monomer to polymer was calculated by the equation

$$\text{Conversion, \%} = \frac{\Delta V \times 100}{m \times K}$$

where K is the contraction coefficient of MMA ($0.22 \text{ cm}^3/\text{g}$) [8], ΔV is the volume change (cm^3), and m is the weight (g) of monomer added. After a certain period of time, the content of the dilatometer was poured into methanol. The obtained polymer was purified by dissolving it in chloroform and precipitating it in methanol several times.

Viscometry

The purified polymer was dissolved in chloroform to prepare a dilute solution for a capillary viscometry of 0.2 g/dL . The efflux time for the polymer solution to flow through a capillary tube was measured by using an Ubbelohde viscometer in a water bath adjusted to $30 \pm 0.1^\circ\text{C}$. The corresponding efflux time of chloroform was 93.07 seconds. However, the viscometry experiment of the MMA-E-7 mixture was carried out at 28°C .

Spectroscopy

UV spectra and NMR spectra of the polymers were collected by a UV spectrophotometer Shimadzu model UV-265 and a Bruker NMR spectrometer (300 MHz) model AMX-300, respectively.

Gel Permeation Chromatography

Gel permeation chromatography (GPC) was carried out with a Waters model R401ALC/GPC using a Styragel 5E-4E-2 column at 30°C at a concentration of 1.0 wt% for 40 minutes running time. The solvent used in GPC work was tetrahydrofuran at a flow rate of 1.0 mL/min .

RESULTS AND DISCUSSION

We carried out radical polymerization of MMA in various solvents, such as benzonitrile, propylbenzene, equimolar mixture of benzonitrile and propylbenzene, and E-7. The selection of isotropic solvents is explained by the chemical structure of E-7, the nematic LC used in this study, which is a mixture of several cyano-4-*n*-alkylbiphenyls [9]. Since these LC materials are basically composed of a benzonitrile unit and an alkylbenzene unit, the equimolar mixture of benzonitrile and pro-

pylbenzene may simulate some interactions such as dipole-dipole, other than any interactions resulted from liquid crystalline structure. As a result, polymerization of MMA in a liquid crystalline solvent is largely different from that in an isotropic solvent. Earlier works [9, 10] reported that the polymerization process in the above isotropic solvents gave rise to chain transfer reactions and a decrease in the molecular weight of polymer.

Figure 1 shows that the initial polymerization rate of MMA in the LC medium is remarkably higher than those in the isotropic solvents. Unlike the polymerization of MMA in benzonitrile and propylbenzene or their equimolar mixture, the polymerization in E-7 proceeds with phase separation as shown in Fig. 2. West [11] reported that a clear phase separation during polymerization of MMA in the presence of LC only occurred at a concentration of more than 30 wt% LC. Furthermore, only PDLC films with a high LC concentration (over 30 wt%) had enough contrast ratio in the UV-cured polyacrylate/LC system [11]. According to Hasebe [12], the microenvironment of the LC droplets affects the mobility of LC molecules in the PDLC system. Ahn and others [13] also revealed that for the clear phase separation of the PMMA-LC systems, the initial PMMA/LC ratio had to be larger than 7/3. This means that the solubility of LC molecules in the polymeric matrix was sufficiently high. Thus, at a comparatively high concentration of LC, the LC molecules captured in the polymer matrix and bound to the MMA macromolecules explain that chain growth and/or chain transfer reactions continued both in the homogeneous polymer phase and at the interfacial boundary between the polymer matrix and the LC domain simultaneously.

Chain transfer reaction of the MMA macroradicals with the LC molecules can be seen by UV spectrophotometry in Fig. 3 and the molecular weight changes shown in Table 1. Figure 3 shows the UV absorption spectra of pure PMMA, PMMA

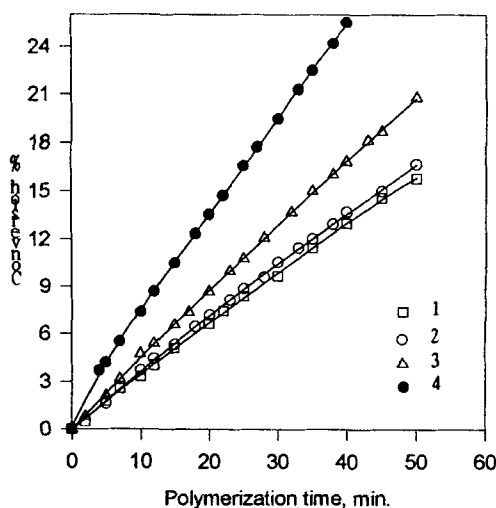


FIG. 1. Reaction conversion of MMA in radical polymerization with different solvents. (1) Benzonitrile, (2) propylbenzene, (3) benzonitrile + propylbenzene (1:1), (4) E-7. Concentration of MMA, 40 wt%; initiator, AIBN, 1 wt%.

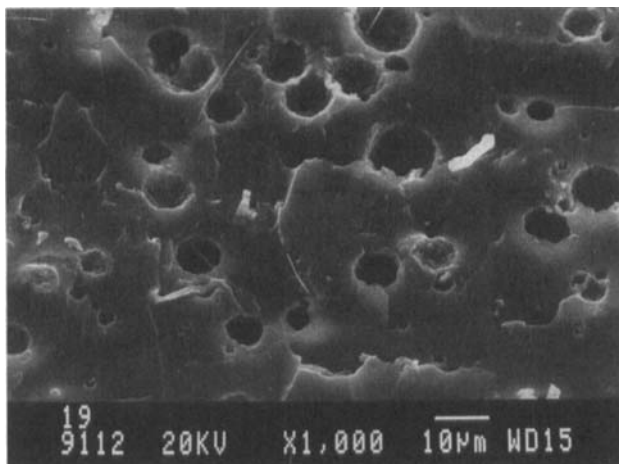


FIG. 2. Scanning electron microscope (SEM) photograph of PMMA film containing 35 wt% of LC.

synthesized in E-7 (44.4 wt%), and the differential spectrum of these two spectra. The polymer samples were carefully purified several times in order to exclude the possibility of impurities. It is clear that the subtraction spectrum (Curve 3) exhibits UV absorption in the 270–290 nm region. The UV absorption of polymer solutions within this range can be explained only by the presence of an aromatic structure in the polymeric chains produced by a chain transfer reaction, such as in Scheme 1.

However, Higashiura [9] did not find benzonitrile units bound to PMMA chains in his investigation. This supports the suggestion that only LC molecules used

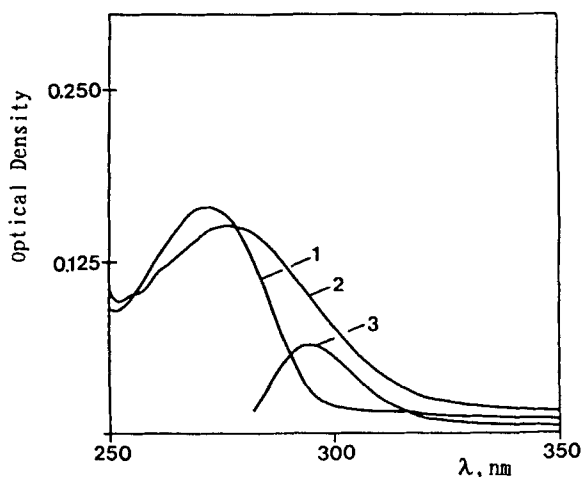


FIG. 3. UV absorption spectra of pure PMMA (curve 1) and PMMA synthesized in the LC medium (44.4 wt%) (curve 2). Curve 3: spectrum (curve 2) subtracted from (curve 1). Concentration of solution, 0.4 g/dL; solvent, chloroform.

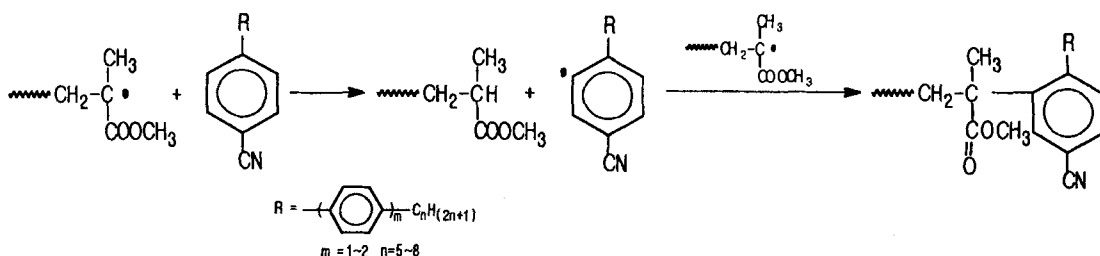
TABLE 1. Effect of Solvent on Molecular Weight of PMMA at Low Conversion

Solvent	Chain transfer constant, $C_s \times 10^4$	Viscosity-average molecular weight, M_η
Benzonitrile	0.162 [10]	162,000
Propylbenzene	0.750	109,000
Benzonitrile + propylbenzene (1:1)	-	126,000
E-7	0.038	339,000

as a solvent medium result in a chain transfer reaction to the MMA macroradicals as suggested in Scheme 1. Table 1 shows that PMMA polymerized in E-7 has the highest viscosity-average molecular weight. This indicates that the LC molecules help to increase the molecular weight of PMMA. As shown in Table 2, a decrease in the viscosity-average molecular weight of PMMA polymerized in E-7 with increasing LC concentration shows that the chain transfer reaction occurs due to the presence of LC. According to the molecular weight data in Tables 1 and 2, it is believed that the molecular weight changes of PMMA and the chain transfer reaction are markedly affected by the solvent nature and the concentration of LC.

Figure 4 shows that the rate of MMA polymerization decreases at low LC concentration. An increase of LC concentration in the mixture from 10 to 40 wt% leads to an increase in the initial polymerization rate and a decrease in the polydispersity of MMA, while the rate of polymerization significantly decreases at higher LC concentration owing to the dilution effect. It is interesting to note that the polydispersity of polymers depends on the LC concentration. Consequently, the presence of LC molecules and the formation of a new phase affect not only the molecular weight of the resulting polymer but also the rate of polymerization and polydispersity of the resulting polymer.

Table 3 presents the solvent variation effect of MMA on the chemical shift of the $^1\text{H-NMR}$ spectra. The chemical shift of MMA changed with the solvent mixed. This means that the solvent molecules surrounding the MMA molecules alter the chemical environment. The chemical shift effects induced by solvent variation may be qualitatively elucidated by the intermolecular interactions between solute and



SCHEME 1. Possible chain transfer reaction between MMA and LC molecules.

TABLE 2. Effect of LC Concentration on the Molecular Weight of PMMA at High Conversion

Initial composition, wt%		Contents of LC in the polymer, wt%	Viscosity-average molecular weight, M_v
MMA	E-7		
100.0	0.0	0.0	1,047,000
83.4	16.6	0.022	741,000
71.4	28.6	0.050	661,000
55.6	44.4	0.075	501,000

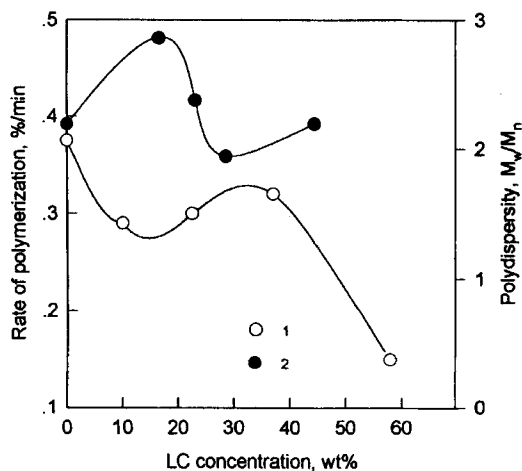


FIG. 4. Dependence of initial polymerization rate (curve 1) and polydispersity (curve 2) of MMA on LC concentration.

TABLE 3. Solvent Dependence of H-NMR Chemical Shifts of MMA

Solvent	Chemical shifts, δ ppm			
	α -H	β -H	CH ₃ O	CH ₃
Chloroform	5.175	5.698	3.354	1.549
Propylbenzene	5.572	6.197	3.750	2.010
Benzonitrile	5.307	5.858	3.479	1.687
Propylbenzene + benzonitrile (1:1)	5.410	5.995	3.583	1.822
E-7	5.489	6.048	3.678	1.880

solvent, such as polarity changes of the C=O and C=C groups. Therefore, an increase in the initial polymerization rate of MMA cannot be understood by simple polarization of the double bonds in MMA molecules by LC molecules because similar effects on the chemical shift are shown by other solvents.

A possible alteration in reactivity due to anisotropic diffusion of monomer molecules in LC medium has been almost unexplored [14]. It is assumed that in the nematic LC phase, diffusion of monomer molecules being polymerized tend to be parallel to the same direction of the LC director at a higher LC concentration [15]. This alignment of monomer molecules may lead to a closer packing of MMA monomers and acceleration of the polymerization rate. Here, formation of ordered structures of LC at a high concentration can be elucidated by measurement of viscosity and surface tension with different compositions of MMA/LC mixtures. Figures 5 and 6 show the relative viscosity and the surface tension of MMA and LC mixture while varying the LC concentration at 28°C, respectively. These figures show that at a relatively high LC concentration, approximately 40–50 wt%, the dependence of relative viscosity and surface tension on the LC concentration becomes larger due to formation of some ordered structures, possibly micelles or domains. At a higher temperature the liquid crystalline order is significantly destroyed, but the LC domains remained as a nucleus able to develop into future LC droplets.

In general the liquid crystalline solvents exhibit molecular ordering and anisotropy, whereas the liquid crystalline nature would be destroyed by being mixed with other substances, such as monomers. Deshpande and Aravindakshan's results [3] are probably correct only at low LC concentrations because they investigated the

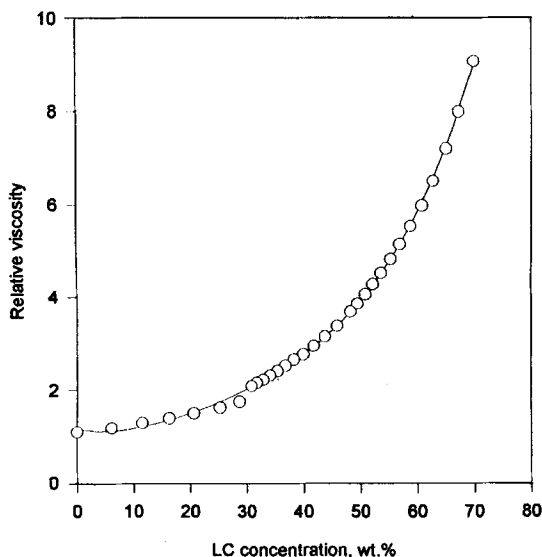


FIG. 5. Relative viscosity of MMA and LC mixture with varying LC concentration at 28°C.

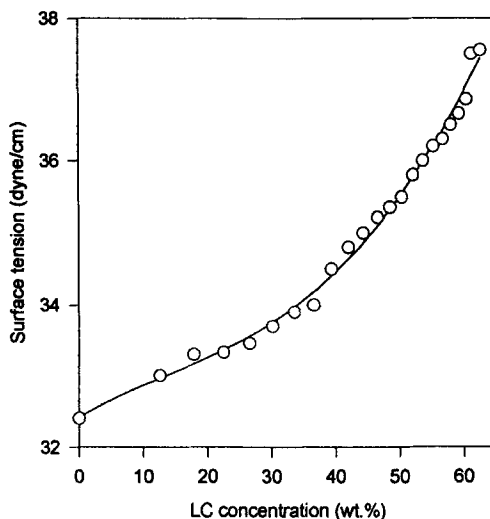
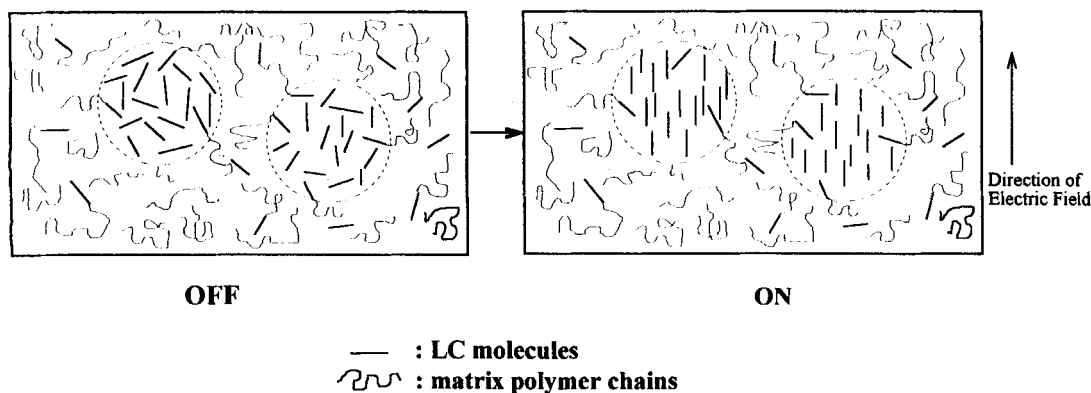


FIG. 6. Surface tension of MMA and LC mixture with varying LC concentration at 28°C.

additives effects of LC, i.e., at a much lower concentration, on the radical polymerization of MMA. Therefore, it is no surprise that the effect of liquid crystalline solvents was not exhibited on the tacticity of the PMMA obtained [3, 4].

An increase in the polymerization rate of MMA in the presence of LC can be explained as follows. An increase of LC concentration in the mixture leads to the faster formation of a LC domain due to an increase of the phase separation rate. Also, the LC domains hold the macroradicals and monomer molecules together for a relatively long period of time due to solubilization [16]. At the same time, the diffusion of the macroradicals on the interfacial boundary is inherently difficult because their mobility is limited by the cage effect. It is assumed that the cooperative interaction between the side chains of PMMA radicals and the alkyl groups of LC molecules onto the LC droplet surface is responsible for enhancing the limitation of chain mobility. Thus, the chain termination reaction is much slower than for a usual case, and the rate of polymerization at the initial stage is accelerated sharply.

Scheme 2 is a schematic drawing of the result of the chain transfer reaction in the MMA/LC PDLC system. The chain transfer reaction results in binding LC molecules to the PMMA polymer chains which exist both in the polymeric phase and on the interfacial boundary. Therefore, it is postulated that some LC molecules in the LC droplets are anchored into the PMMA matrix naturally. Alignment of LC molecules coupled with MMA macroradicals on the interfacial boundary is strongly reduced by chemical anchoring. This may give rise to interference with the orientation of other LC molecules in the LC domain to the electric field direction in the PDLC film, subsequently prolonging the time required for aligning the LC directors to the electric field direction, i.e., response time, in the on-state [17].



SCHEME 2.

CONCLUSIONS

The radical polymerization of MMA in a LC medium results in a phase-separated LC domain-polymer matrix system. An unexpected chain transfer reaction between LC and MMA molecules occurs during polymerization. The rate of polymerization and the polydispersity of the resulting polymer depends on the LC concentration. Formation of the LC domain is attributed to increasing the rate of polymerization and decreasing the polydispersity. It was also found that LC molecules may be able to become completely embedded in the polymer matrix as an isolated molecule or incorporated with PMMA molecules as a macromolecule in the matrix or anchored to the polymer matrix due to chemical bonding to the PMMA molecules. The LC molecules anchored to the polymer matrix may be a major reason why the LC molecules are difficult to align in the direction of an external electric field applied to the PDLC system.

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Received December 16, 1995

Revision received February 25, 1996