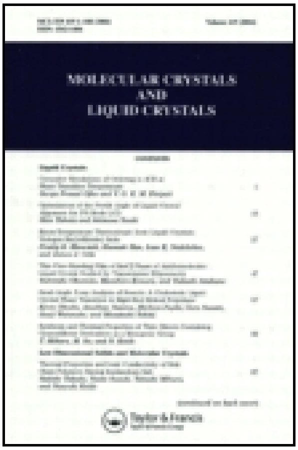

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Role of Molecular Parameters on the Miscibility of Side-Chain Polymer Solutes

G. Sigaud [a] , M. F. Achard [a] , F. Hardouin [a] & H. Gasparoux [a]

[a] Centre de Recherche Paul Pascal, Université de Bordeaux I, 33405, Talence, France

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ROLE OF MOLECULAR PARAMETERS ON THE MISCIBILITY OF SIDE-CHAIN POLYMER SOLUTES

G. SIGAUD, M.F. ACHARD, F. HARDOUIN*, H. GASPAROUX
Centre de Recherche Paul Pascal,
Université de Bordeaux I
33405 Talence, France

Abstract : Binary phase diagrams between a liquid crystalline side chain polymer and a low molecular weight nematogen have been analyzed with regard to their miscibility in the nematic state. Phase separation is frequent in these solutions and varying the chemical structure of the components has strong influence on the critical temperature. In addition, we observe that these mixtures are likely to produce induced smectic A phases the stability of which is similarly influenced by modifications of the molecular parameters.

1. INTRODUCTION

Mixtures of mesogens have been (and still are) extensively investigated for their use in displays[1] and have been (and still are) of great help for the understanding of various fundamental problems (characterization[2],NAC critical points[3] reentrant phases[4], polymorphism of polar compounds[5]...). One can then expect new benefits from the study of mixing a side chain mesomorphic polymer with a low molecular weight (LMW) nematogen. However the analysis of these systems is compli

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**Present address : Laboratoire Léon Brillouin, CEN Saclay 91191 Gif-sur-Yvette, France* cated by the fact that these solutions rarely behave in an ideal manner. They are highly sensitive to little modifications of the chemical constitution of the components which can induce large deviations from the ideal case : such as phase separations and induced smectic A phases as described in the following sections of this paper.

The systems investigated are thus binary mixtures between :

- a rod like LMW nematogen in which three parts can usually be considered as variables : the core and the two tails (Fig. 1).

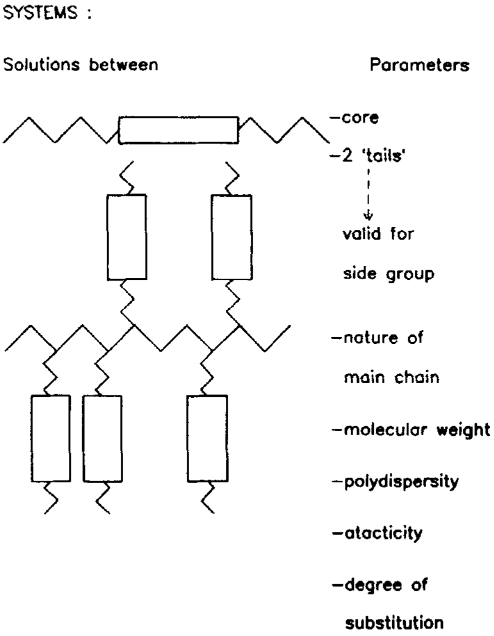


Figure 1

- a side chain polymer which in addition to three possible modifications in the mesogenic pending group (core, spacer and free extremity) offers five other variable parameters : the nature of the main chain, the molecular weight, the polydispersity, the tacticity and the grafting rate.

The study of the distinctive influence of these molecular parameters on miscibility propertie requires that each modification is made under the control of all other parameters.

The technique applied to explore the very large number of diagrams resulting from this methodic approach is the *contact method* already described elsewhere[6]: it is rapid and saves material.

2. CASES OF PHASE SEPARATION

The relevant parameter which we obtain from the contact method to characterize the phase separation is the critical temperature of the consolute point (T_c). The values of T_c are then plotted as a function of the modifications introduced in the structure of one of the components of the mixture (Fig. 2).

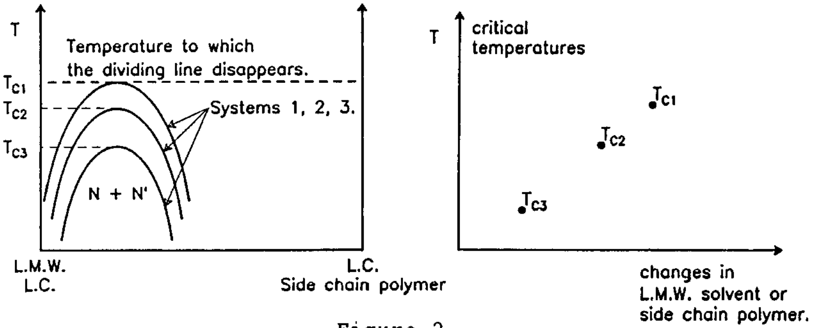


Figure 2

2.1) Study of phase separation at constant backbone :

The main chain used at this end is a polymethylsiloxane (PMS). This choice is driven by two reasons :

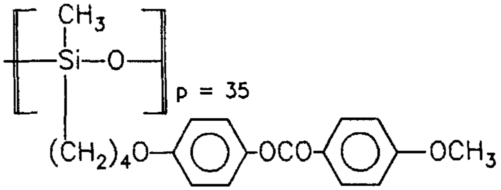
- Side-chain PMS were reported first to induce nematic-nematic gaps of miscibility[7,8].
- As the synthesis of these polymers is made through a substitution on a hydrogeno PMS available with reproducible specifications, one can easily control the molecular weight and polydispersity of the final material.

Thus, these PMS are convenient to study :

- the influence of variations in the solvent given the polymer (backbone and side group).
- the influence of variations in the side group given the solvent.

2.1.1. Modifications in the solvent :

- We use the following constant PMS[9] :

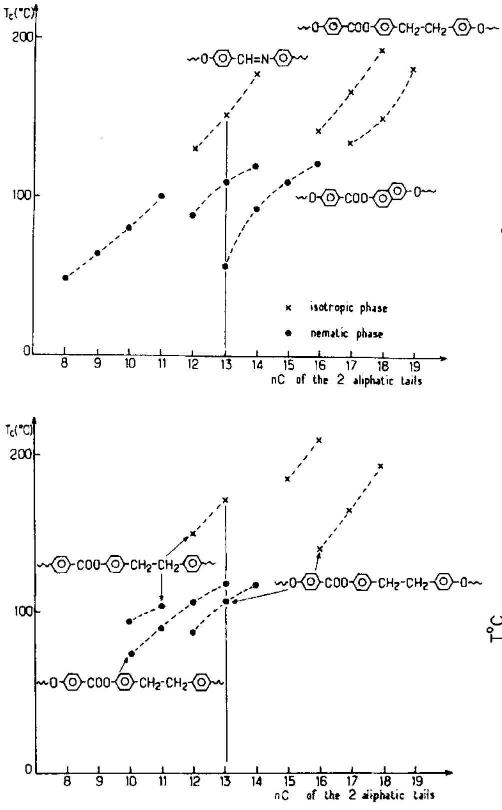


$P_{4,1}$

S_A ~75°C N ~104°C I

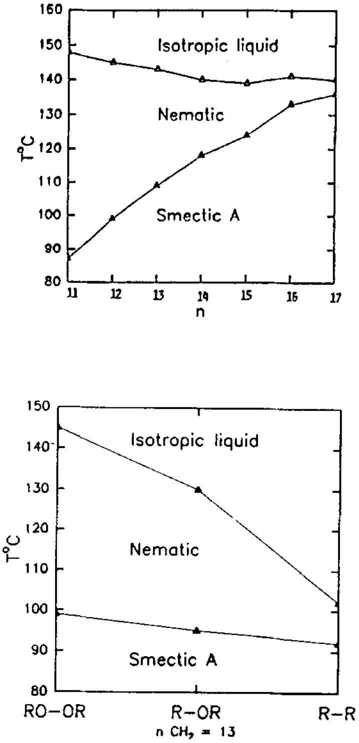
- Different families of solvents with different cores have been used. In each family we have varied the lengths of the aliphatic tails and then plotted T_c as a function of the total aliphatic content of the solvent (n CH_2) (Fig. 3a and 3b).

The regular increase of T_c with increasing n[10] (Fig. 3a and 3b) and the evolution at constant n from one series to another (eg Fig. 3b) can be related to the decrease of the smectogenic character (T_{NA} compared to T_{NI}) of the solvent (Fig. 4a and 4b).



Figures 3a and 3b

Evolution of the critical temperature versus the aliphatic content in different series of solvents. (X : phase separation in the isotropic liquid - o : phase separation in the nematic phase).



Figures 4a and 4b

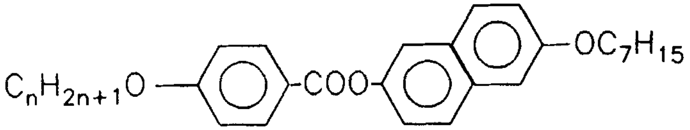
Evolutions of the nematic-isotropic and nematic-smectic A temperature of transition

a) in the series of naphtalene derivatives (3a)

b) from one series to the other (solid line 3b)

2.1.2. Modifications in the side group :

- In this case the investigations are made at constant series of solvents[11] :



- The influence of the flexible part have been mainly analyzed.
- Influence of the length of the spacer (Fig. 5) : a more flexible spacer lowers T_c (decoupling from the backbone favours the solubility).

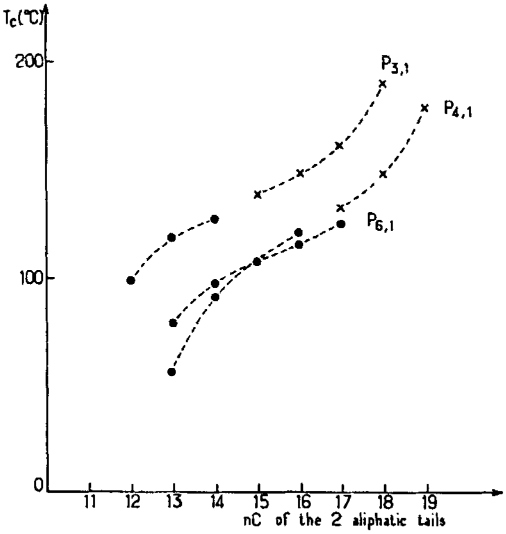


Figure 5 – crosses and dots : see figure 3

- Influence of the length of the free extremity (Fig. 6) : the lengthening of this part which is related to a loosening of the pair associations among the side groups of different chains results in a decrease of T_c too[12].

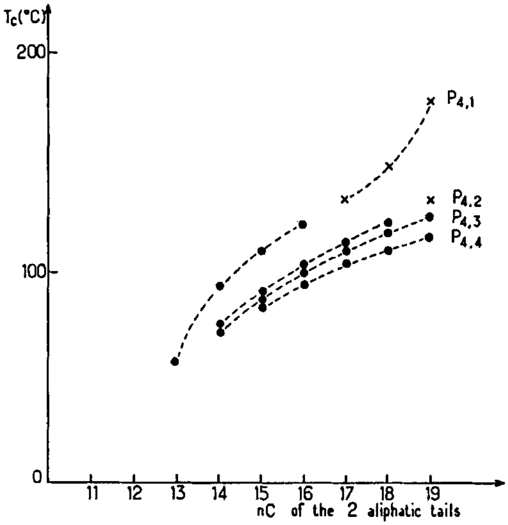
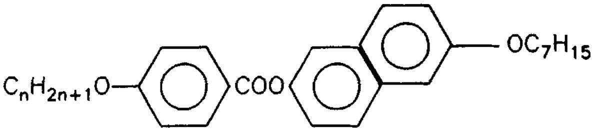


Figure 6 - crosses and dots : see figure 3

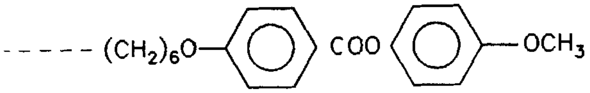
2.2) Study of phase separation with different backbones

It was of great importance to give evidence that immiscibility is not a singular characteristic of PMS.

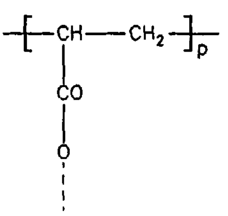
This part has been performed using a constant series of solvents :



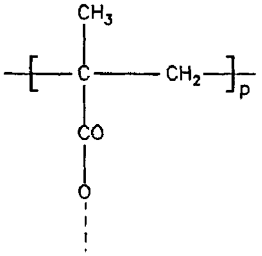
The same side group :



has been grafted on two different backbones :



Polyacrylates[13]



Polymethacrylates[14]

Of course, the main result is that gaps of miscibility are observed with these two types of polymers as well. Qualitatively, the effect of the solvent is similar to what is observed with PMS backbones (Fig. 7).

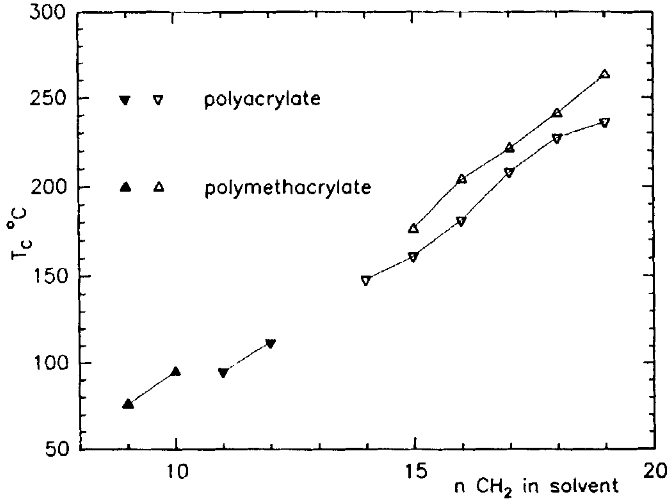


Figure 7

empty triangles : phase separation in the isotropic liquid

filled triangles : phase separation in the nematic phase

Can we compare T_c from one material to the other from a quantitative point of view ? In fact we cannot directly attribute the entire variation of T_c to the only change in nature of the backbone. Changing from PMS to PA and PMA implies to take also in account a change in molecular weight and in polydispersity (see table 1). At this point it appears worth looking at the effect of the molecular weight (M_w).

	M_w	I
PMS	13600	<1.2
PA	25000	>2
PMA	354000	>2

Table 1[15] - I : index of polydispersity

The figures 8a and 8b present the influence upon T_c of variations of M_w for two samples of PMS and two samples of PA. Either the difference in T_c is small (for PMS) or null (for PA) : this attenuation may be connected to the larger polydispersity of the PA samples.

PMS_a M_w= 12600 I<1.2

PMS_b M_w= 28700 I<1.2

PA_a M_w= 6000 I>2

PA_b M_w= 25000 I>2

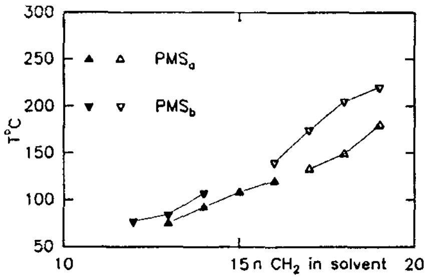


Figure 8a

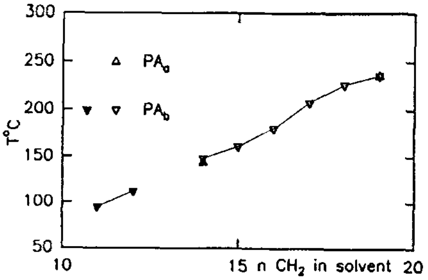


Figure 8b

Empty and filled triangles : see figure 7

Owing to this limited effect of mass one can try a comparison between a PA and a PMS sample bearing the same side group (Fig. 9) which shows no large difference in T_c at constant solvent.

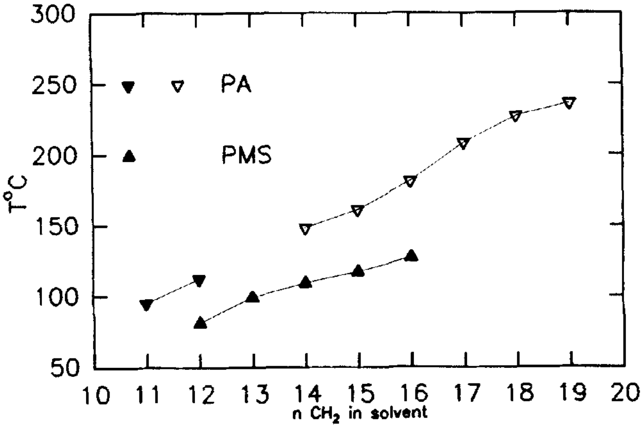


Figure 9 - empty and filled triangles : see figure 7

The comparison of the effects of modifications in the side group makes also sense : a decrease of T_c is observed for a lengthening of the spacer or of the free extremity in the case of PA or PMA backbones as is the case with PMS.

To conclude this section on phase separation one can note that substituting polar side groups has a spectacular effect whatever the main chain is : complete immiscibility is observed in the given series of non polar solvents used in this work. A detailed discussion of the effect of polarity will be disclose in a forthcoming communication.

3) CASES OF INDUCED SMECTIC A PHASES

Binary mixtures of low molecular weight mesogens mostly exhibit simple eutectic type phase diagrams (Fig. 10a). Sometimes a domain of induced smectic A phase is injected in a given range of molar fractions (Fig. 10b) : polar/non polar binary mixtures are more likely to exhibit this non ideal behavior which is really uncommon with non polar/non polar systems.

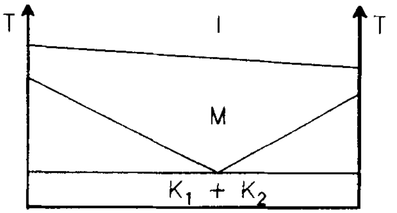


Figure 10a

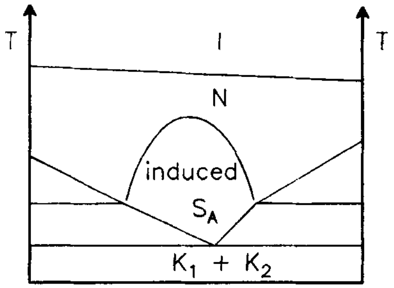


Figure 10b

In contrast, induced S_A are easily observed in blends of a LMW and a liquid crystalline side chain polymer. This is the case when a polar LMW and a non polar polymer are mixed. But, although more unexpected, it is now often observed in binary diagrams of a non polar LMW and a non polar polymer.

Using the contact method, these enhanced smectic phases can be characterized by their temperatures at the maximum, T_{SA}. The influence of the molecular parameters of the components on the phenomenon is then analyzed plotting T_{SA} as a function of the structural modification as done for T_c. So, since the variables are the same, a direct comparison between the evolutions of T_c and T_{SA} is possible.

For example the figure 11 shows that T_{SA} increases with increasing aliphatic content of the solvent (i.e. : increasing smectogenic character of the solvent) and that T_{SA} decreases with increasing length of the spacer in the side group : T_{SA} and T_c respond qualitatively in the same way to these structural modifications.

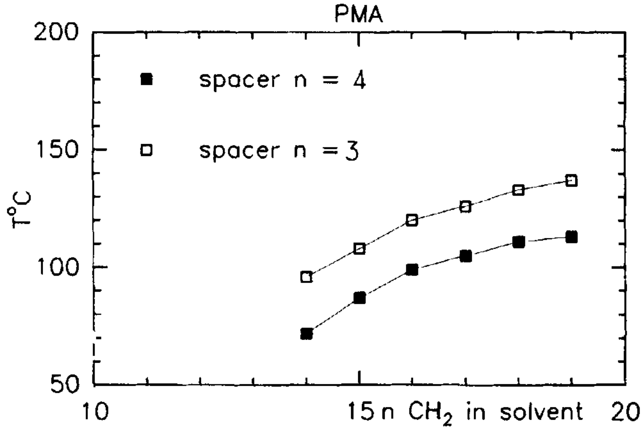
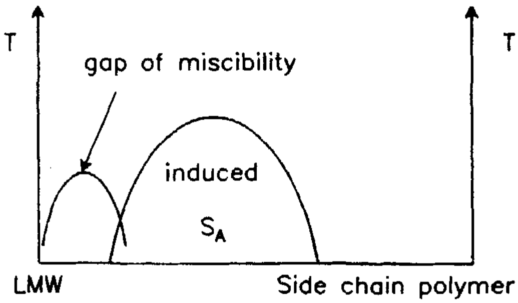


Figure 11 - Temperature at the maximum of induced smectic A phase as a function of the aliphatic content of the solvent (same series as in 2.2)

Moreover an induced smectic A and a gap of miscibility can coexist in the same diagram :



But this observation depends on the structural characteristics of the solvent (Fig. 12).

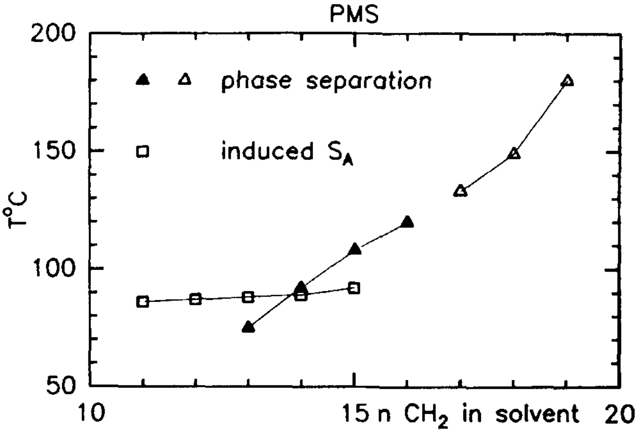


Figure 12 - empty and filled triangles : see figure 7

4) CONCLUSION

The main results of these works can be summarized as follows :

- The phase separation occuring in solutions of a side chain polymer and a LMW solvent is not an exclusive feature of the polymethylsiloxane backbone. The miscibility is soundly affected by any modification of the side group susceptible to change the conformation and/or its dipolar distribution.
- Induced smectic A phases are non ideal behaviors as frequent as phase separation in these systems.

Both respond in a similar way to molecular modifications and they compete in some systems. So, the relevant interactions responsible for these phenomena might be connected in some manner as assumed by DUNMUR et al[16].

- At last, we point out that, among the numerous binary systems investigated so far, we never observed phase separation with laterally attached side groups on a PMS backbone[17].

One may wonder wether the phase separation is characteristic of liquid crystalline comb polymers.

REFERENCES

1. G.J. Sprokel, "The Physics and Chemistry of Liquid Crystal Devices". Plenum Press, New York, 1979
2. H. Sackmann, D. Demus, Mol. Cryst. 2, 81 (1966)
3. S. Chandrasekhar, Journal of Stat. Phys. 34, 883 (1984)
4. P.E. Cladis, Phys. Rev. Lett. 35, 48 (1975)
5. F. Hardouin, A.M. Levelut, M.F. Achard, G. Sigaud, Journal de Chimie Physique, 80, 53 (1983)
6. G. Sigaud, M.F. Achard, F. Hardouin, M. Mauzac, H. Richard, H. Gasparoux, Macromolecules, 20, 578 (1987)
7. H. Ringsdorf, H.W. Schmidt, A. Schneller, Makromol. Chem., Rapid Comm., 3, 745 (1982)
8. C. Casagrande, M. Veyssie, H. Finkelmann, J. Phys. (Paris), 43, L-371 (1982)
9. M. Mauzac, F. Hardouin, H. Richard, M.F. Achard, G. Sigaud, H. Gasparoux, Eur. Polym. J. 22, 137 (1986)
10. H. Benthack-Thoms, H. Finkelmann, Makromol. Chem., 186, 1895 (1985)
11. H.T. Nguyen, 7th Conference of Socialist Countries, Halle, GDR (1985)
12. M.F. Achard, F. Hardouin, G. Sigaud, M. Mauzac, Liq. Cryst., 1, 203 (1986)
13. P. Keller, Macromolecules, 20, 462 (1987)
14. L. Noirez, J.P. Cotton, F. Hardouin, P. Keller, M. Lambert, F. Moussa, G. Pepy (to be published)
15. L. Noirez, private communication
16. D.A. Dunmur, R.G. Walker, P. Palffy-Muhoray, Mol. Cryst. Liq. Cryst., 122, 321 (1985)
17. F. Hessel, H. Finkelmann, Polymer Bulletin, 14, 375 (1985)