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Synthesis and Charactrization of Polycaprolactone Nanocomposites Reinforced with Montmorillonite

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ABSTRACT

[DEACOOH]-Montmorillonite intercalations complex obtained from Na-Montmorillonite and 10-Carboxy-n-decyldimethylethylammonium bromide (organic cation) was reacted with the monomer (ε-caprolactone) to achieve the [DEACOOH]-ε-caprolactone-Montmorillonite intercalations complex. From this intercalations complex Montmorillonite/Polycaprolactone nanocomposites in which montmorillonite (inorganic polymer) is chemically linked with the polycaprolactone (organic polymer) were formed at 240°C by three different methods such as in stoichiometric amounts between monomer and organic cation, in excess of only the monomer and in excess of both organic cation and monomer. The products obtained after polymerization were analyzed with X-ray diffractometer and TEM.

Key words : [DEACOOH]-Montmorillonite intercalations complex, Na-Montmorillonite, 10-Carboxy-n-decyldimethylethylammonium bromide, ε-caprolactone, Organic cation

1. Introduction

Montmorillonite which belongs to the smectite group[1,2] is a layered silicate of mica type[3,4] and used very widely in forming intercalations complexes of clay as well as in industry because of the increasing ability of its own volume by one-dimensional innercrystalline swelling,[5,6] especially there exists a exchangeable metal cation in the interlayer space of montmorillonite. Therefore if this metal ion would be replaced with an organic cation which has at least one long chain by a cation exchange reaction, organophilic montmorillonite intercalations complexes which have different material properties could be formed. This kind of organophilic montmorillonite can be used not only as a filler for lacquer, greese, cosmetics, paint, etc.,[3] but also in refining a factory waste water which is contaminated by organic compounds,[7,8] it will also be used as a model system with which its behavior under various different conditions could be proved.[9-11]

If the organic cation has a long chain with an organic functional group and organic monomer polymerizes with this functional group after it is additionally intercalated between the silicate layers, a composite in which inorganic and organic polymer are chemically bonded, i.e. a clay-polymer nanocomposite can be synthesized by the chemical linking of the organic cation as a counter ion for the clay layers which have an anionic electrical charge with the organic polymer.[12-16] In this kind of composite the organic polymer will not be separated from the clay under any solvent in which it is soluble except acid. Otherwise, i.e. in case that clay (inorganic polymer) and the organic polymer are not be chemically bonded, the organic polymer will be separated from the clay under the solvent in which it is soluble, and then the resultant clay-polymer nanocomposites can not play role as a composite any more. These nanocomposites can be used, for example, as an automobile bumper, and it will have an excellent stability because of the absorbing effect of the impact, a good economical efficiency because of the long durability and take part in the protection of environment because of the reduction of the waste plastics.

Poly(ε-caprolactone) (PCL) is a kind of biodegradable aliphatic polymer and is recently being much researched for use in pharmaceutical controlled release systems, medical devices and in degradable packaging.[17-19] Especially PCL has a very excellent commercial use as a copolymer with polyvinylchloride, acrylonitrile-butadiene-styrene, etc.,[20-23] but the future development for the potential use of this PCL is much limited, because it has a low melting point and glass transition temperature (Tg). Therefore it could be applied in the various fields, if its mechanical properties can be improved by reinforcing it with reinforcements or fillers such as clay.

In this research we have tried to synthesize montmorillonite-polycaprolactone complex in which the inorganic polymer (montmorillonite) is chemically linked with the organic polymer(polycaprolactone) in order to achieve such a plastic (PLC) composite reinforced with montmorillonite. For this purpose we have substituted the metal ion, sodium ion (Na^+) with the following organic cation with long alkyl chain to ensure an enough reaction space for the chemical reaction between the montmorillonite layers at first;

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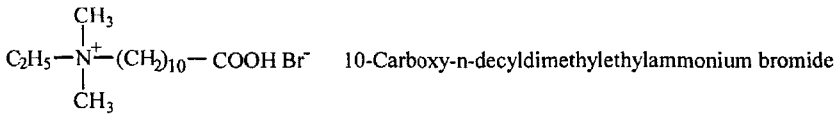

10-Carboxy-n-decyldimethylethylammonium bromide

(will be abbreviated as [DEACOOH] Br after now)

After the organic monomer (ε-caporlactone) has been intercalated into the layers of this [DEACOOH]-Montmorillonite intercalations complexe polymerization of the monomer was proceeded at 240°C by three different methods such as in stoichiometric amounts between monomer and organic cation, in excess of only the monomer and in excess of both, organic cation and monomer, and the so formed inorganic-organic complexes in which the montmorillonite as an inorganic polymer is chemically combined with the polycaprolactone as an organic polymer.

2. Experimental Procedure

2.1. Materials

n-undecanoic acid bromide and dimethylethylamine for the preparation for the organic cation and ε-caprolactone as starting material for the organic polymer were commercially obtained from Fluka and/or Aldrich. Ca-bentonite from Schwaiba, Germany was chemically refined to achieve Na-Montmorillonite.

2.2. Method

2.2.1. Formation of the Organophilic [DEACOOH]-Mont Intercalations Complex

Water solution of the [DEACOOH] Br was added to the water suspension of Na-Montmorillonite under stirring. The whole mixture was then left at 65°C for 48 h under occasional stirring and thereafter centrifuged so that the swelling solution can be isolated from the product, the organophilic [DEACOOH]-Mont intercalations complex. This [DEACOOH]-Mont was washed with dist. water and then dried at 100°C in oven at first and continuously at 65°C in vacuum of 10^{-2} torr for 24 h.

2.2.2. Formation of [DEACOOH]-ε-Caprolactone-Montmorillonite

In the 100 mL round flask the stochiometrical amounts of the organophilic [DEACOOH]-Mont and ε-caprolactone were well mixed with mortar, and then the mixture was left under N_2-atmosphere for 30 min under occasional stirring. Thereafter the round flask with the mixture was heated at 95°C (oil bath) for 30 min, cooled slowly up to 50°C, and well mixed with mortar. Then the sample was put into the reaction flask again, left under N_2-atmosphere for 30 min with occasional stirring, heated at 95°C for 30 min, cooled slowly up to 50°C and left at this temperature for 3 days. This procedure was repeated 3 times more.

2.2.3. Formation of Montmorillonite/Polycaprolactone Nanocomposites

The formation of montmorillonite/polycaprolactone nanocomposites in which montmorillonite (inorganic polymer) and polycaprolactone (organic polymer) are chemically linked were attempted using [DEACOOH]-ε-caprolactone-Montmorillonite intercalations complex by three different methods such as in stoichiometric amounts between monomer and organic cation, in excess of only monomer and in excess of both organic cation and monomer.

The starting materials were put into the thick horosilicate ampule which was preheated with heat gun to remove the moisture, and then the ampule (including sample) was evacuated, sealed and heated at 240°C for 48 h for the polymerization.

2.2.4. Characterization

The X-ray diffraction analyses on the pure Na-Montmorilloniteas as a starting material, the organophilic [DEACOOH]-Montmorillonite intercalations complexes and montmorillonite/polycaprolactone nanocomposites in stoichiometric amounts between monomer (ε-caprolactone) and organic cation, in excess of only the organic cation and in excess of both, organic cation and monomer were performed with X-ray diffractometer (Philips Novelco and XPERT PRO) using Cu K_α-radiation (λ = 1.5418 Å).

The obtained montmorillonite/polycaprolactone nanocomposite was also analyzed with transmission electronic

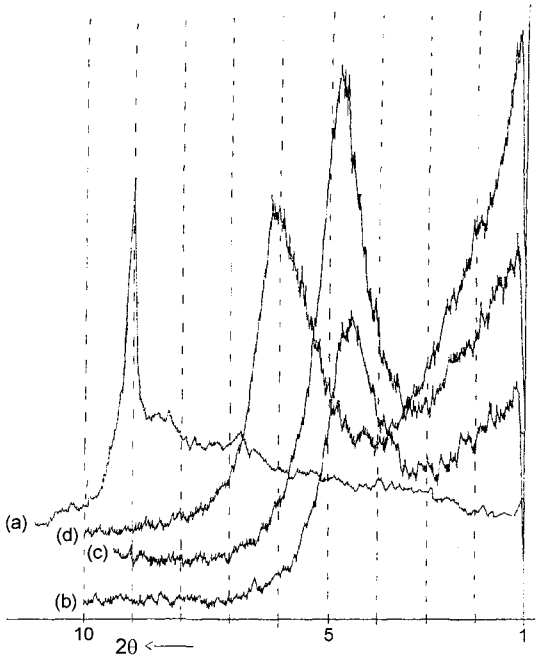

Fig. 1. X-ray diffraction patterns of [DEACOOH]-Mont. (a) Na-Montmorillonite dried in high vacuum at 65°C 24 h, (b) after 48 h exchange-time, under exchange solution, (c) after eight times washing, under water, and (d) after 24 h drying in high vacuum at 65°C.

microscope (TEM; JEOL 100 LX with 100 kV Accelerating Voltage).

3. Results and Discussion

3.1. Results of [DEACOOH]-Montmorillonite/[DEACOOH]-ε-Caprolactone-Montmorillonite

The organophilic [DEACOOH]-Mont intercalations complex obtained from the reaction between Na-Montmorillonite and [DEACOOH] Br by the cation exchange reaction was characterized with an X-ray diffractometer under the following conditions:

(A) The equilibrium solution after cation exchange reaction was centrifuged; the solid residue was analyzed with X-ray diffractometer under still wet condition with the adherent equilibrium solution (Fig. 1(b)).

(B) Thereafter the centrifuged solid residue was washed eight times with distilled water until it was free from halide and characterized with X-ray diffrectometer under still wet condition with water (Fig. 1(c)).

(C) The washed sample was dried at 65°C for 24 h in high vacuum (10^{-3} torr) and analyzed with X-ray diffractometer under the dried condition in high vacuum (Fig. 1(d)).

The obtained results from the measurements with X-ray diffractometer are summarized in Table 1 which shows us that the basal spacing values between the starting material, Na-Montmorillonite, and the reaction products, [DEACOOH]-Mont, are quite different. The Na-Montmorillonite used as a starting material swells toward infinitely under distilled water, i.e. the layers of the crystals separate to the individual layers. So the attractive interactions between the adjacent layers will reduce. After drying it under high vacuum its basal spacing falls to 9.8~10.1 Å. The X-Ray Diffraction (XRD) patterns for the summarized data in Table 1 are demonstrated in Fig. 1.

In case of [DEACOOH]-Mont the basal spacing of 19.6 Å is obtained under the exchange solution, but it lies on 18.5 Å with the reduction of 1.1 Å after washing eight times with water until it was free from halide. Under this condition it is obvious that the sample has still much water between the layer of the intercalations complex. Therefor the sample was dried at 65°C in high vacuum (10^{-3} torr) for 24 h, whereafter the closed packing was obtained and the basal spacing also decreased upto 14.50 Å with the reduction of 4 Å. It is a comprehensible value, because the density of charge of montmorillonite used in this research is very small. Under such density of charge the alkyl ammonium ions with up to at least 12 C-Atom numbers form a flat lying monolayer, as we know from many other researches.

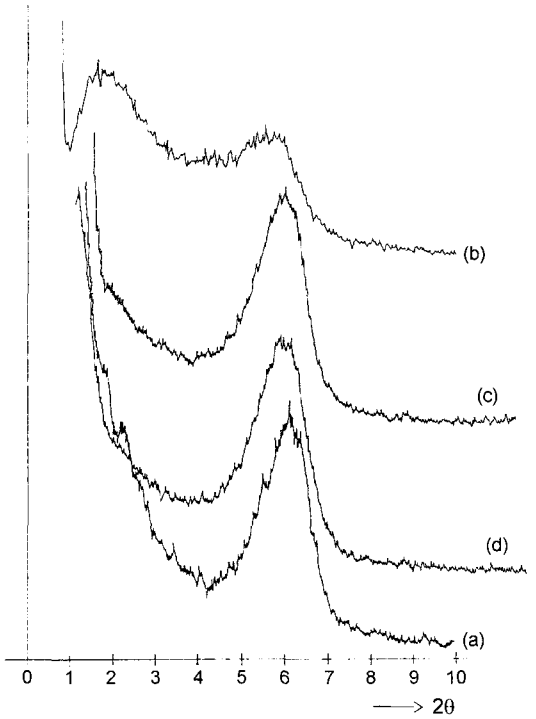

Fig. 2. X-ray diffraction patterns of [DEACOOH]-Mont with ε-caprolactone. (a) [DEACOOH]-Mont as a starting material, (b) after intercalation of ε-caprolactone into [DEACOOH]-Mont, (c) after drying of (b) in high vacuum right after the exchange reaction, and (d) after extraction with methanol and following drying in high vacuum of (b).

Fig. 2 shows the XRD-patterns for the [DEACOOH]-ε-caprolactone-Montmorillonite synthesized by the reaction between the organophilic [DEACOOH]-Mont intercalations complex and ε-caprolactone. As shown in Fig. 2 the XRD pattern of the [DEACOOH]-ε-caprolactone-Montmorillonite is quite different from that of the starting materials, the organophilic [DEACOOH]-Mont intercalations complex. This suggests that the caprolactone is successfully intercalated into the layer of [DEACOOH]-Mont. But from Fig. 2 we can see that the XRD patterns obtained after drying in high vacuum directly after the cation exchange reaction and after extraction with methanol and the following drying in high vacuum are almost the same as that of the starting material, the organophilic [DEACOOH]-Mont intercalations complex. This suggests that the intercalated ε-caprolactone between the layers of [DEACOOH]-Mont are extensively removed again from the layers.

Table 1. Basal Spacings(Å) Measured after the Cation Exchange Reaction

Sample treatment	Basal spacing(Å) of	
	Reaction product	Na-Montmorillonite
After more than 48 h exchange time, under exchange solution	19.62	-
After eight times washing, measured under water	18.54	Toward infinitely
After 24 h drying in high vacuum at 65°C	14.54	9.8~10.1

Table 2. Results of Polymerization of ε-Caprolactone by Three Different Reaction Methods

Sample treatment	Basal spacings(Å) [DEACOOH]-caprolatone-Mont. as a starting material	Basal spacings(Å) after olymerization at 240°C for 48 h		
		In stoichiometric amount	In excess of monomer	In excess of monomer & organic cation
Before polymerization	50.72			
After polymerization, extraction with methanol & drying in high vacuum at 65°C, 24 h	14.53	48.18	51.74	62.17

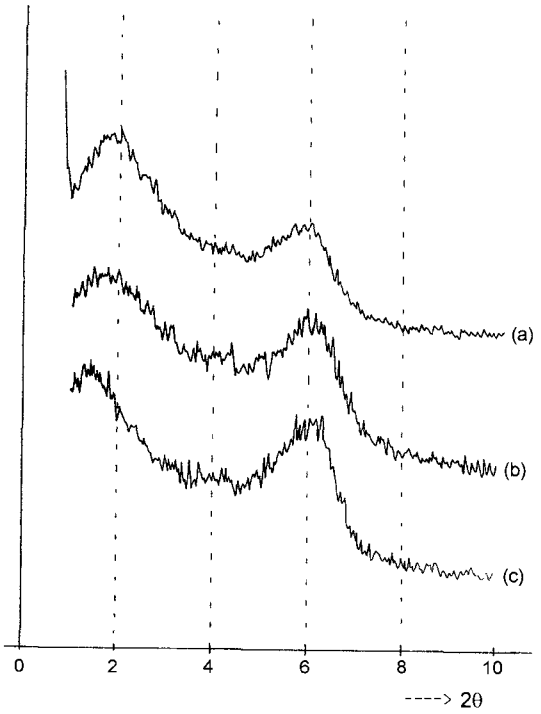

Fig. 3. X-ray diffraction patterns after polymerization. (a) in stoichiometric amount between monomer and organic cation, (b) in excess of only monomer, and (c) in excess of both components, monomer and organic cation.

3.2. Results of the X-Ray Analyses after Polymerization

From the results of Table 2 and X-ray diffraction patterns in Fig. 2 we can see that ε-caprolactone was almost fully removed from the layers of [DEACOOH]-Mont, if the caprolactone was not polymerized in the layers, dried at 65°C for 24 h in high vacuum directly after intercalation reaction (Fig. 2(c)) and after extraction with solvent (here methanol for example) (Fig. 2(d)). But the results of Table 2 and Fig. 3 show that the ε-caprolactone was not removed from the layers after the polymerization. This suggests that the polymerization of ε-caprolactone is successfully performed.

In the second column of the Table 2 the basal spacings of the reaction products, [DEACOOH]-Caprolactone-Montmorillonites, which were synthesized by the intercalation reaction of ε-caprolactone into the [DEACOH]-Mont and will be used as a starting material for the polymerization of the organic monomer are summarized. The basal spacing of [DEACOOH]-Caprolactone-Montmorillonite before polymerization was 50.72 Å, but it was reduced to 14.53 Å after extraction with solvent, methanol, in which the monomer is soluble and the following drying in high vacuum of 10^{-2} torr at 65°C for 24 h. This is caused by the removal of almost all monomer (ε-caprolactone) from the layers.

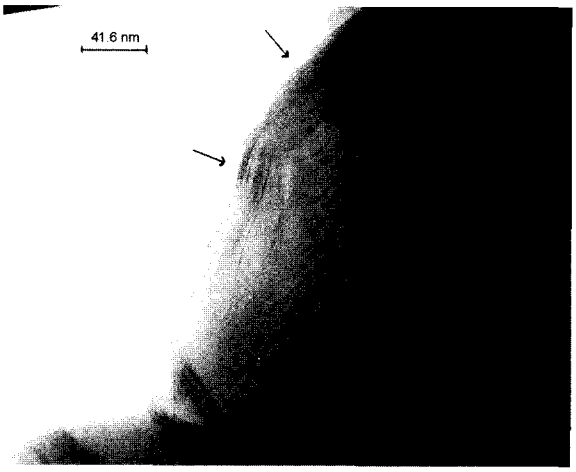

Fig. 4. TEM picture of the montmoriilonite/polycaprolactone nanocomposite.

In the next column of the Table 2 the basal spacings of the products obtained after polymerization at 240°C for 48 h in stoichiometric amount between monomer and organic cation, in excess of only monomer and in excess of both, monomer and organic cation are summarized. From the results of the Table 2 and Fig. 3 we can see that the basal spacing increases with the amount of monomer and organic cation. After extraction of the polymerized products with methanol and the following drying in high vacuum of 10^{-2} torr at 65°C, for 24 h the basal spacing is 48.18 Å for the polymerization in stoichiometric amount between monomer and organic cation, while the basal spacings measured after polymerization in excess of only monomer and in excess of both, monomer and organic cation, are 51.74 Å and 62.17 Å, respectively. From these results it is obvious that the polymerization has been successfully proceeded and the basal spacing becomes wider with the excess amount of the monomer and the organic cation.

3.3. Results of Transmission Electronic Microscopy (TEM)

In order to observe the appearance of the clay mineral as a reinforcement in the polymerized product this polymer was investigated with transmission electronic microscope (Fig. 4). From Fig. 4 we can observe the repeating arrangement

of the layers of the reinforced montmorillonite in the polymer matrix.

4. Conclusions

In this research [DEACOOH]-Montmorillonite intercalations complex obtained from Na-Montmorillonite and 10-Carboxy-n-decyldimethylethylammonium bromide (organic cation) was reacted with the organic monomer (ε-caprolactone) to achieve the [DEACOOH]-ε-caprolactone-Montmorillonite intercalations complex. From this intercalations complex Montmorillonite/Polycaprolactone Nanocomposites in which montmorillonite (inorganic polymer) is chemically linked with the polycaprolactone (organic polymer) were formed at 240°C by three different methods such as in stoichiometric amounts between monomer and organic cation, in excess of only monomer and in excess of both, monomer and organic cation and the following results were found:

1. As a result of X-ray diffraction analysis under wet condition for the [DEACOOH]-Montmorilonite after the cation exchange reaction the basal spacing of 19.62 Å has been obtained.

2. The basal spacing obtained after eight times washing with dist. water until it was free from halide was 18.54 Å.

3. The basal spacing measured after drying in high vacuum of 10^{-2} torr at 65°C for 24 h was 14.54 Å.

4. The basal spacings for the samples obtained after the extraction of the polymerized products and the following drying in high vacuum of 10^{-2} torr at 65°C for 24 h lie from 48.18 to 62.17 Å, while the basal spacing for the starting material before polymerization lies on 14.53 Å under the same condition.

5. Especially we could observe that the basal spacing becomes higher with the excess amount of the monomer and the organic cation.

6. The repeating arrangement of the layers of the reinforced montmorillonite in the polymer matrix was also observed by TEM.

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REFERENCES

1. H. Wiberg, "Textbook of Inorganic Chemistry(*in Ger.*)," pp 91-100, *Berlin; New York; de Gruyter*, 1985.
2. M. I. Rozengart, G. M. Vyunova, and G. V. Isagulyants, "Layered Silicates as Catalysts," *Russian Chem. Rev.*, **57** [2] 115 (1988).
3. A. Weiss, "Organic Derivatives of Mica-Type Layer-Silicates(*in Ger.*)," *Angew. Chem.*, **75** 113 (1963).
4. G. Lagaly and A. Weiss, "Arrangement and Orientation of Cationic Tenside on Silicate Surfaces (IV. Arrangement of n-Alkylammonium Ions in Case of Low Loaded Layer Silicates(*in Ger.*))," *Angew. Chem.*, **68** [2] (1956).
5. U. Hofmann, "From the Chemistry of High Swellable Clays (*in Ger.*)," *Angew. Chem.*, **68** [2] 53-80 (1956).
6. U. Hofmann, "From the Chemistry of Clays," *Angew. Chem.*, **80** [18] 736-47 (1968).
7. K. Kuhn, "Influence on Sorption Properties of Organophilic Bentonites(*in Ger.*)," Diplomarbeit, University of Munich 1985.
8. K. Kuhn and A. Weiss, "Investigations of the Capability of Solvents by the Organophilic Bentonites(*in Ger.*)," *Schriftenreihe Angew. Geol.* Karlsruhe **4** 141-59 (1988).
9. S. J. Cho and J. O. Kim, "A Study of Intercalations-Complexes of Montmorillonite as Model-Systems (I)," *The J. of Nat'l Sci.*, PaiChai Uniniversity, **5** [1] 77-86 (1992).
10. S. J. Cho, Y. S. Ko, I. G. Kim, and W. C. Oh, "A Study of Intercalations-Complexes of Montmorillonite as Model-Systems (II)," *J. Kor. Ceram. Soc.*, **30** [4] 259-64 (1993).
11. S. J. Cho, "A Study of Intercalations-Complexes of Montmorillonite as Model-Systems (III)," *J. Kor. Ceram. Soc.*, **38** [5] 431-37 (2001).
12. Z. Wang and T. J. Pinnavaia, "Hybrid Organic-Inorganic Nanocomposites : Exfoliation of Magadiite Nanolayers in an Elastomeric Epoxy Polymer," *Chem. Mater.*, **10** 1820-26 (1998).
13. J. W. Gilman, "Flammability and Thermal Stability Studies of Polymer Layered-Silicate(Clay) Nanocomposites," *Appl. Clay Sci.*, **15** 31-49 (1999).
14. X. Kornmann, H. Lindberg, and L. A. Berglund, "Synthesis of Epoxy-Clay Nanocomposites," *ANTEC '99*, 1623-27.
15. J. X. Li, J. Wu, and C. M. Chan, "Thermoplastic Nanocomposites," *Polymer,* **41** 6935-37 (2000).
16. X. Fu and S. Qutubuddin, "Synthesis of Polystyrene-Clay Nanocomposites," *Mater. Latt.,* **42** 12-5 (2000).
17. M. Vert, S. M. Li, G. Spenlehauer, and P. Guerin, "1. Bioresorbability and Biocompatibility of Aliphatic Polyesters," *J. of Mater. Science-Mateials in Med.,* **3** [6] 432-46 (1992).
18. R. Langer, "New Methods of Drug Delivery," *Sci.*, **249** 1527-33 (1990).
19. S. Lannace, N. de Luca, and L. Nicolais, "Physical Characterization Incompatible Blends of Polymethylmethacrylate and Polycaprolactone," *J. Appl. Polym. Sci.*, **41** 2691-704 (1990).
20. R. de Juana and M. Cortazur, "Study of the Melting and Crystallization Behavior of Binary Poly(ε-Caprolactone)/Poly(Hydroxy ether of Bisphenol A)," *Blends Macromolecules*, **26** 1170-76 (1993).
21. G. Detieuw, G. Groeninckx, and H. Reynaers, "Miscibility and Morphology of Binary Polymer Blends of Polycaprolactone with Solution-Chlorinated Polyethylenes," *Polymer,* **30** [4] 595-603 (1989).
22. G. Detieuw, G. Groeninckx, and H. Reynaers, "Miscibility, Crystallization and Meeting Behaviour, and Morphology of Binary Blends of Polycaprolactone with Styrene -co-Maleic Anhydride Copolymers," *Polymer,* **30** [12] 2158-63 (1989).
23. J. Heuschen, R. Jerome, and P. Teyssie, "Polycaprolactone-Based Block Copolymers II : Morphology and Crystallization of Copolymers of Styrene or Butadiene and ε-Caprolactone," *J. Polym. Phys.*, **27** 523-44 (1989).