Synthesis and properties of polyacetylene–polynorbornene–polyacetylene triblock copolymers

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Polyacetylene-*block*-polynorbornene-*block*-polyacetylene triblock copolymers were made via the Durham precursor route using a dititanacyclobutane living metathesis catalyst. I.r. and u.v.-v.i.s. spectroscopic investigations on stretch-oriented copolymer films show high anisotropies with polarized light. The copolymers stay soluble if the thermal conversion is carried out in solution. Electron micrographs using different imaging systems (TEM, STEM, SEM) and thermal analysis data show phase separation between domains of the different polymer blocks.

(Keywords: living polymerization; polyacetylene triblock copolymers; phase separation)

INTRODUCTION

Since the discovery that the electrical conductivity of polyacetylene (PA) films was enhanced by many orders of magnitude on chemical doping with oxidative or reductive agents[1,2], this polymer has been of interest to experimentalists and theorists for many reasons. However, these studies have always been hampered by its poor processability (insoluble, intractable, unmeltable) and environmental instability. In order to improve these problematic properties research has focused on the synthesis of block and graft copolymers[3,4] and blends[5]. Some of those showed irregular phase separation[6–8]. Other examples of block copolymers have shown that well ordered small domains can result as a consequence of phase separation[9,10]. The majority of the studies in this field have been carried out on A–B–A type triblock copolymers with hard (high T_g) A segments and soft (low T_g) B segments. As an example polystyrene-*block*-polybutadiene-*block*-polystyrene (PS–PB–PS) systems show highly ordered spherical, rodlike or lamellar structures[11]. The structure and dimensions of these domains are determined by the size of the segments in the copolymers and by the method of sample preparation.

The construction of structures consisting of conducting and semi-conducting domains having dimensions of <100 Å has resulted in major advances in solid state science. These superlatices or 'quantum dots' have been constructed by mechanical deposition of the requisite materials.

Recent advances in the polyacetylene synthesis via ring opening metathesis polymerization (ROMP) (precursor routes[12–14], living polymerization[15–17]) allow the preparation of materials that contain the chemical structures necessary to form the required morphology to mimic these mechanically prepared structures. In this paper a new synthesis of polyacetylene-*block*-polynorbornene-*block*-polyacetylene (= PA–PN–PA) triblock copolymers and their characterization are presented. Results of electron microscopic (TEM, STEM) and thermoanalytical (d.s.c.) investigations are presented to demonstrate phase separation between PA and PN domains.

The synthetic pathway is shown in *Scheme 1*. Starting with the bifunctional metathesis catalyst **1** the central block of PN is formed in the first step, the outer blocks of the PA precursor blocks are made in the second step. The number of repeat units in each block is predetermined by the molar ratio of initiator and monomer. This method allows variations of the block size within a broad range.

EXPERIMENTAL

Polymer synthesis

The synthesis of the bifunctional metathesis catalyst followed the method described previously[17]. In a typical experiment (e.g. copolymer 5 in *Table 1*) 0.96 mmol norbornene was added by vacuum transfer to the

Table 1 Copolymer characteristics

Copolymer no.	Monomer ratio (m:2n:m)[a]	$M_{n,th}$	$M_{n,exp}$[b]	Polydispersity	T_g(°C)
1	45:48:45	20.700	27.500	2.45	—
2	50:190:50	35.900	35.400	1.53	51
3	85:163:85	45.600	44.900	1.63	55
4	75:100:75	36.400	62.100	1.45	61
5	115:223:115	62.400	62.900	1.34	—
6	88:415:85	71.700	70.900	1.31	48

[a] Compare structure **2** in *Scheme 1*
[b] Determined by g.p.c. calibrated against polystyrene standards

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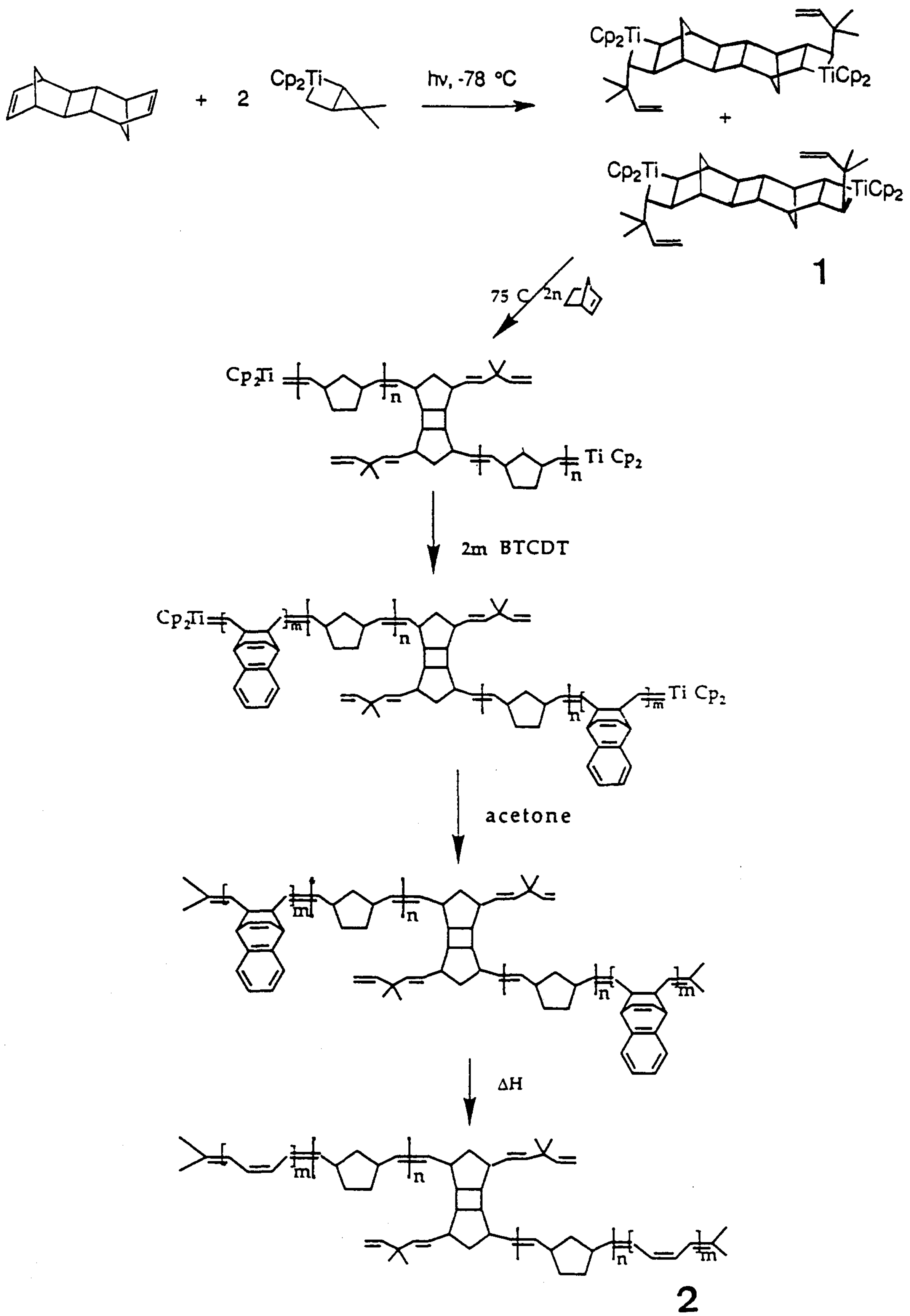

Scheme 1

catalyst solution (*c.* 0.005 mmol in 0.5 ml d_8-toluene). The polymerization was carried out at 75°C. As soon as the conversion was >95% (determined by ^1H n.m.r.) the second monomer (7,8-benzo-tricyclo[4.2.2.0^{2,5}]deca-3,7,9-triene, 180 mg, 1 mmol) was added. After *c.* 20 min the second monomer was almost quantitatively consumed, and the reaction was stopped by adding dry, deoxygenized acetone to endcap the living polymer ends in a Wittig-type reaction. The polymer solution was diluted with 5 ml toluene, flash chromatographed over silica, and the polymer precipitated by dropwise addition of the solution to a >3-fold excess of ethanol. If the polymer was still slightly yellow, this purification step was repeated. After drying the polymer *in vacuo*, the typical overall yield was 60–90% in different reactions. Reduced yields occurred occasionally because of cross-linking due to the addition of an excess of diolefin or over-irradiation in the initiator synthesis. These cross-linked polymers resulting from the side reaction were separated during the flash chromatography.

Polymer characterization

Prior to thermal treatment the average molecular mass (M_n, M_w) and the polydispersity index (PDI, M_w/M_n) of each prepolymer were determined by means of size exclusion chromatography using methylene chloride as the eluent. Three columns (Shodex KF 803, 804 and 805, calibrated against polystyrene standards) were used in series.

Films were cast from 0.1 to 2.0% prepolymer solutions in toluene or THF on a suitable substrate (glass, NaCl or KBr slide) for spectroscopic (i.r., u.v.-v.i.s. and Raman) and SEM investigations. The precursor polymers were converted to PA at 120–140°C *in vacuo*. Stress was applied with a spring to produce stretch-oriented films. After thermal treatment, TEM specimens were prepared from films made as described above if the films were thin enough (in some cases thin films were cast directly on the grids) and investigated without further treatment (staining with OsO_4 by hanging the grid into the vapour over a 2% aqueous solution or over fresh OsO_4 for 2–15 min did not yield any noticeable change in contrast). In some cases good results were obtained with WF_6 as the staining/doping agent. Specimens for SEM investigations were coated with gold or carbon prior to analysis. The thickness of these samples was between 1 and 10 μm. Doping was carried out with iodine in the gas phase. D.c. conductivity was determined using a standard 4 point probe technique. Solution-u.v. and n.m.r. spectra were taken from solutions in toluene or d_8-toluene respectively before and after heating to 120°C.

RESULTS AND DISCUSSION

In the synthesis of the PA–PN–PA block copolymers the PA/PN ratio and the absolute block size were varied, see *Table 1*. The molecular weight could be well controlled by variation of the catalyst/monomer ratio. The soft PN segment was always made larger than the hard PA segments in order to favour the phase separation of conducting PA in a PN continuous matrix. All precursor polymers were readily soluble. Sometimes an insoluble polymer partition was received, which was separated by flash chromatography. This side reaction result from degenerated catalyst sites formed by over-irradiation in the synthesis of the bifunctional catalyst **1**. If the photochemical step was followed by n.m.r. the reactions could be terminated when the formation of the difunctional initiator was complete, and the catalyst reacted selectively with the cyclic olefins. Backbiting or branching at the vinyl groups in the central starting unit (compare *Scheme 1*) was not observed, the catalyst behaved as a living system. Homogeneous films could be cast from solutions in toluene or THF from the copolymers purified by reprecipitation. The resulting films have a smooth surface, even though the polymer tends to concentrate at the borderline of the wetted area. U.v.-v.i.s. and i.r. spectra were taken from films prepared by this technique.

U.v.-v.i.s. spectra of the precursor polymers showed no absorption above 300 nm, however, thermal treatment (at 130°C *in vacuo* or under Ar) generated absorption maxima in the region of 450 nm. This shift of the absorption maximum is related to the formation of long sequences of conjugated double bonds. In *Figure 1*, u.v.-v.i.s. spectra of amorphous (graph a) and stretched (graphs b and c) films of copolymer 6 are shown. The orientation of the PA-sequences in the stretch-oriented films was investigated by polarized light spectroscopy. In both the disordered and stretch-oriented films the absorption maximum is observed around 480 nm which is at significantly higher energy compared to pure PA films made via the Durham–Graz method[18], which has the absorption maximum around 600 nm. The anisotropy of the optical absorption was also lower. This effect might be due to disordered regions at the PA/PN interface of the separated domains (e.g. out of plain torsion, internal strain, defects, etc.). A more detailed discussion concerning the evaluation of conjugation length in these copolymer systems based on Raman spectroscopy is given in reference 19. Graph d shows a u.v. spectrum obtained by heating the prepolymer in solution in toluene to 110°C for several hours. The polymers remained dissolved. Only comparatively short sequences of conjugated double bonds are found corresponding to a conjugation length of *c.* 5–10 double bonds (determined according to the method of Kohler[20]). This low number might be due to sp^3 defects or kinks from rotation around single bonds in the polymer thus disturbing the π-conjugation along the chain.

From such a solution in toluene-d_6 n.m.r. spectra were taken (see *Figure 2*). The broad peaks around 2.7 ppm, 3.9 ppm and 6.6 ppm from the PA precursor disappear, the naphthalene peaks come into the spectrum. The PN part remains almost unchanged. No peaks typical for PA were recorded, probably because of the rigidity of the PA chains.

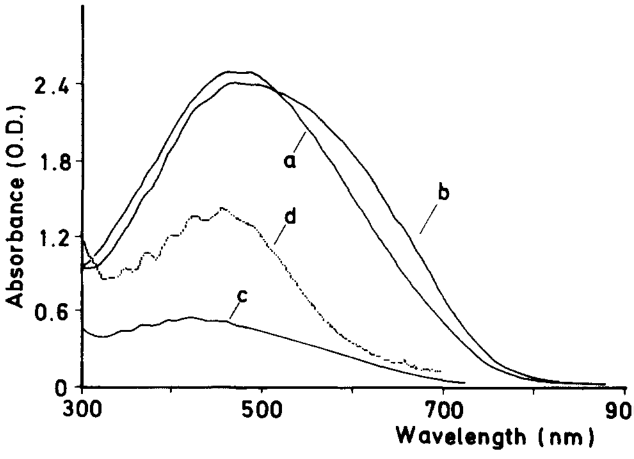

Figure 1 U.v.-v.i.s. spectra of copolymer 6 after thermal extrusion of naphthalene at 130°C. Curve (a) amorphous film; curve (b) oriented film (draw ratio 4) polarized parallel to drawing direction (sample between polarizer and analyser, both parallel); curve (c) same film as curve (b), polarized orthogonal to drawing direction; curve (d) same copolymer, converted at 110°C in toluene in a closed n.m.r. tube

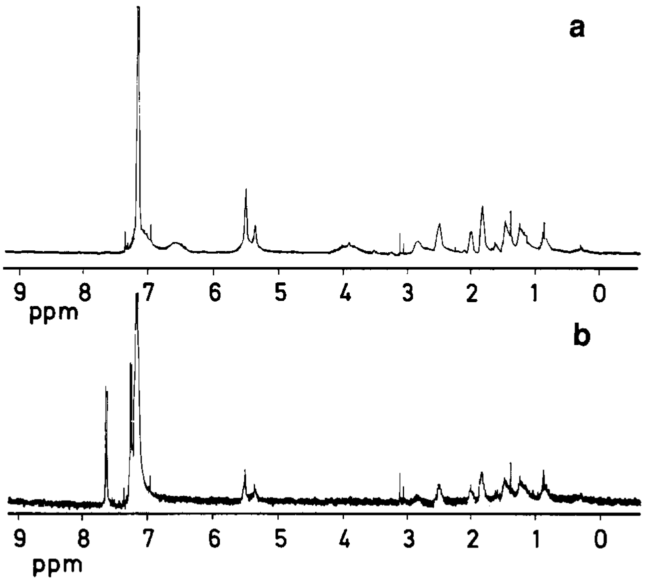

Figure 2 ^1H n.m.r. spectra of copolymer 6 in toluene-d_6, (a) before conversion, (b) after conversion at 110°C in toluene in a closed n.m.r. tube

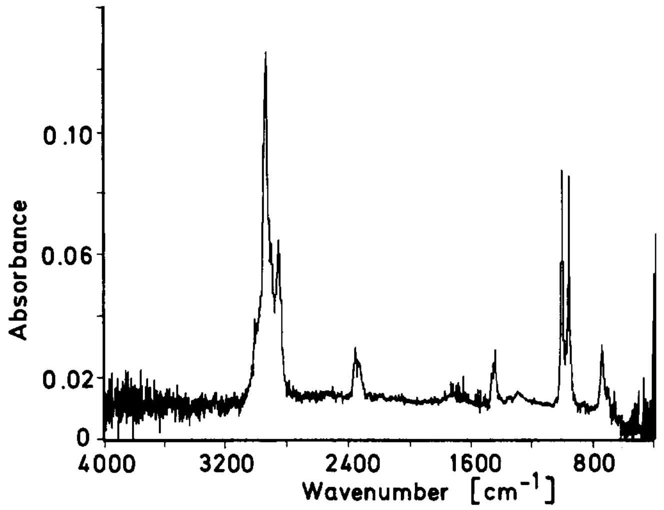

Figure 3 I.r. spectrum of a thin film of copolymer 6

The i.r. spectrum of a converted copolymer film is shown in *Figure 3*. It compares well to spectra of PN/PA blends. The most prominent bands result from long conjugated sequences of E-double bonds (1010 cm^{-1}) from the PA partition and separated E-double bonds (966 cm^{-1}) from the PN partition. No remaining aromatic bands were detected, indicating that the naphthalene extrusion had been completed during the thermal conversion of the PA precursor. In stretch-converted films the quality of orientation of the polymer chains is demonstrated by the polarized i.r. spectrum, the important section of which is shown in *Figure 4*. The degree of orientation is much higher for the PA partition than for the PN part of the copolymer. This has been deduced from the anisotropy of the out of plane vibrations of the different ethenylene units at 1010 cm^{-1} and 966 cm^{-1} respectively. More details of spectra of amorphous and of highly ordered stretched films with high anisotropies are included in reference 19.

The converted films show a shiny metallic appearance

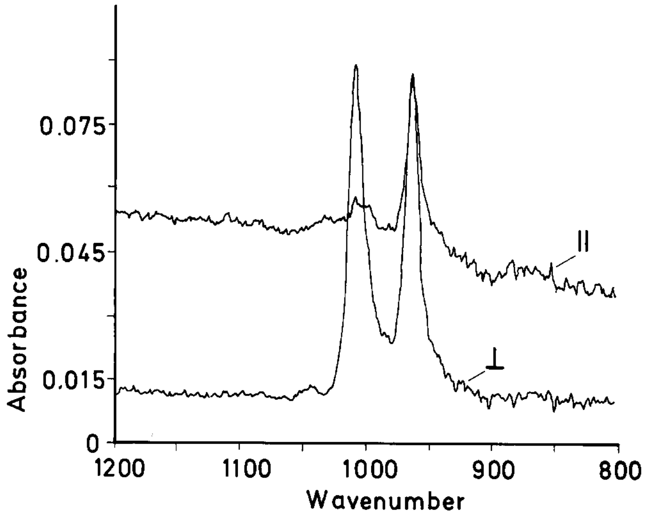

Figure 4 I.r. spectrum (section) of an oriented film of copolymer 6, light polarized as in *Figure 1*

and are not soluble anymore; the black colour remained for several days under ambient conditions before complete oxidative bleaching occurred. The d.c. conductivity of freshly prepared films is that of an insulator. After doping with iodine, the d.c. conductivity of the copolymer films always reaches values of about 10^{-5} S cm^{-1}, which is somewhat lower than the value measured for nonconjugated elastomers[21–25] treated heavily with iodine. Because no conductivity data for doped PN were available, we exposed PN films to iodine vapour. Again an increase of the conductivity to the same final value of *c.* 10^{-5} S cm^{-1} was measured. Because this behaviour is not clearly explained by means of current models about doping of nonconjugated unsaturated polymers, further details must be investigated and will be published later[26]. The similar values for the different copolymers and pure PN are consistent with complete separation of the conjugated PA domains by a polynorbornene matrix.

In *Figure 5* d.s.c. plots of copolymer 2 are shown. Freshly prepared polymers show a T_g in the region of 40–60°C (see *Table 1*) as expected for PN, and two broad exothermic peaks: the small one at 140 is the *Z/E* isomerization of already created PA double bonds, while the larger one results from the thermal elimination of naphthalene. After aging the polymers for 1–3 months, the T_g cannot be observed in the first run, while an endothermic peak shows up around 70°C, which is in good agreement with a melting point for PN. After 2–3 heating circles (not higher than 100°C in order to avoid thermal conversion of the PA precursor) the melting point disappeared and the T_g at the original temperature was observed. This thermal behaviour can only be interpreted with phase separated PN domains. After thermal conversion no T_m or T_g was observed. This indicates crosslinking during the conversion.

In *Figure 6* the transmission micrograph of an iodine doped film of copolymer 4 cast directly on the grid is shown. Irregularly distributed dark domains distributed in a continuous matrix can be seen. These domains are ascribed to PA. As we already succeeded in getting good electron diffraction pattern of stretch-oriented Durham PA[22] we investigated a stretched film of copolymer 5 (draw ratio 5) in a TEM. The electron diffraction pattern, shown in *Figure 7*, clearly indicates crystalline PA. The

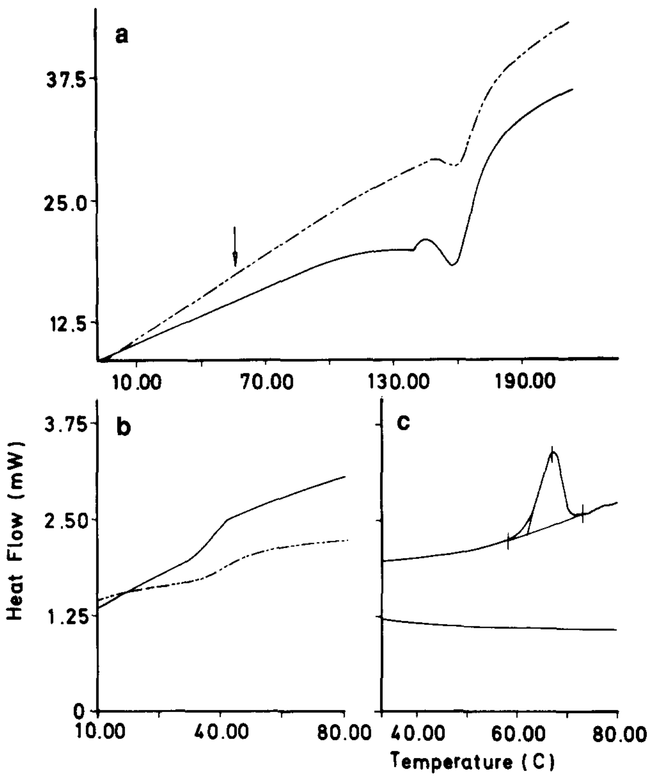

Figure 5 (a) D.s.c. plot of a pure PA-precursor polymer (——), and d.s.c. plot of copolymer 3 (—··—), the arrow marks the T_g; (b) d.s.c. plot of copolymer 3, freshly prepared sample; (c) d.s.c. plot of the first run of the same copolymer aged for *c*. 3 months

Figure 6 TEM micrograph of copolymer 4 doped with iodine, film cast directly on a grid; black bar equals 200 Å

same film was doped with WF_6 and investigated with an STEM and, as expected for PA domains, dark spots are observed. In addition cloudy stripes along the drawing direction, a fine lamellar structure, indicated by an arrow in *Figure 8*, is seen. These are ascribed to oriented regions which yielded the diffraction pattern. Scanning with a secondary electron detector (SE) gave pictures with a similar texture.

In SEM micrographs of thicker films structures with much bigger spheric domains were observed sometimes indicated by surface bladders of almost identical diameters distributed regularly all over the copolymer surface

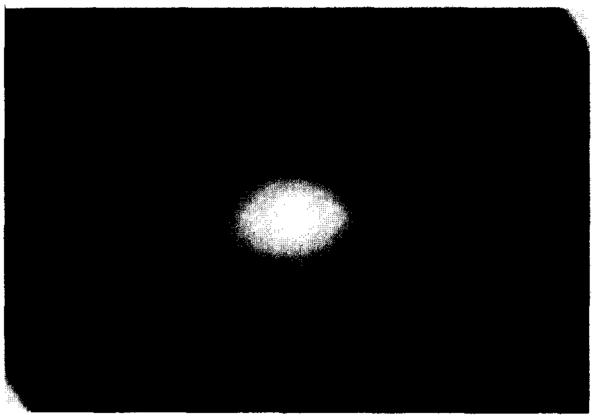

Figure 7 Electron diffraction pattern of copolymer 6

Figure 8 STEM micrograph of an oriented film of copolymer 6, stained with WF_6; dark domains indicate PA

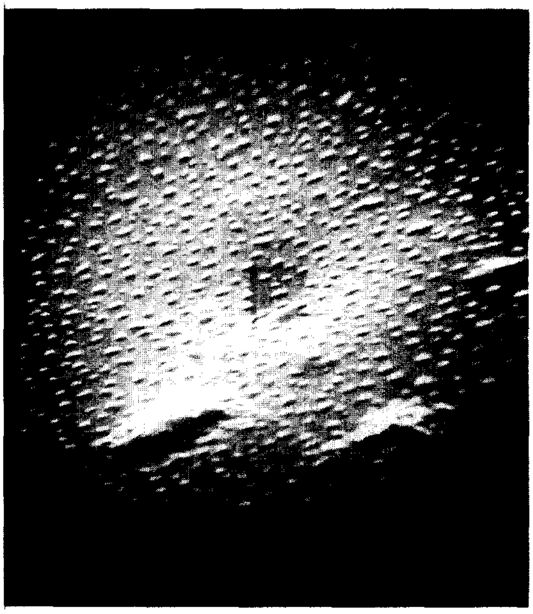

Figure 9 SEM micrograph of a *c*. 3 μ thick film of copolymer 5 doped with iodine

especially after doping (see *Figure 9*). Carbon coated doped films also showed regularly distributed domains, which appear as light dots because of their metallic behaviour. PN homopolymer prepared in the same way as the copolymer did not show similar microdomains, but showed a much more structured surface.

CONCLUSIONS

Polyacetylene-*block*-polynorbornene-*block*-polyacetylene (PA–PN–PA) triblock copolymers with well defined block sizes can be synthesized via the Durham-precursor route using difunctional living metathesis catalysts. Films made from such polymers show phase separation which remains after thermal conversion. Separated domains of PA and PN have been observed. Oriented films show some crystallinity and anisotropies similar to neat Durham–Graz PA. This offers new possibilities for the field of molecular electronics, if better ways to control the phase separation can be developed. To date quantum size effects could not be observed.

The precursor copolymers may also be converted in a 0.1% solution in benzene in a sealed tube. Then the converted polymer remains dissolved. Thus the synthesis of block copolymers may be named as another method to produce soluble PA.

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REFERENCES

1 Berets, D. J. and Smith, D. S. *Trans. Farad. Soc.* 1968, **64**, 823

2 Chiang, C. K., Heeger, A. J. and MacDiarmid, A. G. *Ber. Bunsenges. Phys. Chem.* 1979, **83**, 407

3 Stowell, J. A., Ammas, A. J., Beevers, M. S. and Farren, T. R. *Polymer* 1989, **30**, 195

4 Krouse, S. and Schrock, R. R. *Macromolecules* 1988, **21**, 1888 and references

5 Lee, K. I. and Jopson, H. *Makromol. Chem., Rapid Commun.* 1983, **4**, 375

6 Bates, F. S. and Baker, G. L. *Macromolecules*, 1983, **16**, 707

7 Armes, S. P. and Vincent, B. *Synth. Met.* 1988, **25**, 171

8 Lee, K. I. and Jopson, H. *Makromol. Chem., Rapid Commun.* 1983, **4**, 375

9 Kämpf, G. 'Habilitationsschrift' TH Aachen, Germany, 1977

10 Kämpf, G. *Progr. Colloid Polym. Sci.* 1975, **57**, 249

11 Keller, A., Pedemonte, E. and Willmouth, F. M. *Nature*, 1970, **225**, 538

12 Edwards, J. H. and Feast, W. J. *Polymer* 1980, **21**, 595

13 Feast, W. J. and Winter, J. N. *J. Chem. Soc., Chem. Commun.* 1985, 202

14 Stelzer, F., Brunthaler, J. K., Leising, G. and Hummel, K. *J. Mol. Catal.* 1986, **36**, 135

15 Murdzek, J. S. and Schrock, R. R. *Organometallics* 1987, **6**, 1373

16 Gilliom, L. and Grubbs, R. H. *J. Mol. Catal.* 1988, **46**, 255

17 Risse, W., Wheeler, D. R., Cannizzo, L. F. and Grubbs, R. H. *Macromolecules* 1989, **22**, 3205

18 Leising, G. *Synth. Met.* 1989, **28**, D215; *Phys. Rev. B* 1988, **38**, 10313

19 Verdon, T., Leising, G. and Stelzer, F. *Synth. Met.*, in press

20 Kohler, B. E. *Springer Series in Solid State Sciences* 1985, **63**, 100

21 Thakur, M. *Macromolecules* 1988, **21**, 661

22 Cholli, A. L. and Thakur, M. *J. Chem. Phys.* 1989, **91**, 7912

23 Shang, Q.-Y., Pramanick, Sh. and Hudson, B. *Macromolecules* 1990, **23**, 1886

24 Suh, D. H. and Wnek, G. E. *Polym. Prepr.* 1990, **31**, 410

25 Borman, S. *Chem. Eng. News* 1990, **68/20**, 53

26 Leising, G. and Stelzer, F., unpublished results

27 Kahlert, H., Leising, G., Leitner, O., Uitz, R. and Stelzer, F. in *Proc. 17th Int. Conf. Physics of Semiconductors* (Eds J. D. Chadi and W. A. Harrison) Springer, New York, 1985, p. 1453