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Methacrylic polymers bearing side-chain permanent dipole azobenzene chromophores spaced from the main chain by chiral moieties: synthesis and characterization

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Abstract

Novel optically active polymethacrylates bearing in the side chain a chiral group of one prevailing absolute configuration linked to the *trans*-azoaromatic chromophore, have been synthesized by radical homopolymerization of the corresponding optically active monomers, prepared in turn from optically active precursors by synthetic methods avoiding any racemization of the chiral center. These polymeric derivatives, namely poly[(*S*)-3-methacryloyloxy-1-(4′-X-4-azobenzene) pyrrolidine], with X = CN, CHO, CH=C(SO_2CH_3)(CN), CH=C($CN)_2$, are characterized by the presence of the 3-hydroxy-pyrrolidinyl ring as the chiral moiety and the azoaromatic donor-acceptor conjugated system as the moiety with permanent dipole moment. The polymers display optical activity in solution much higher than that afforded by the corresponding low molecular weight models, representative of the monomeric repeating unit, purposely synthesized. Owing to the substantially stereoirregular structure of the main chain, this suggests that the overall optical activity is mainly due to conformational dissymmetry of the macromolecules. Spectroscopic evidence suggests the presence in the above mentioned polymeric derivatives of dipole–dipole interactions between the side-chain azoaromatic chromophores, occurring as a consequence of their anchorage to the polymer backbone, which favors their aggregation.

Keywords: Photochromic chiral polymers; Donor-acceptor conjugated systems; Azobenzene-containing polymers

1. Introduction

The presence of conformational dissymmetry in polymeric methacrylates bearing a chiral group interposed between the main chain and the *trans*-azoaromatic photochromic chromophore can be detected by chirooptical techniques, such as circular dichroism (CD), suitable to reveal the existence of chiral perturbation induced by the chiral moieties onto the electronic transitions of the achiral aromatic chromophore. This allows to observe the presence of dichroic bands at the absorption wavelength of the aromatic chromophore in the related spectral region. Thus, depending on the conformational stiffness of the chiral spacer, remarkable dichroic effects were previously observed in polymethacrylate esters when the chiral group was able to give hydrogen bonding, such as in derivatives bearing the L-lactic acid group linked through ester and secondary amide bonds to the backbone and the azoaromatic chromophore [1], respectively, as well as when the chiral group was a rigid cyclic moiety, such as in the case of (*S*)-2-hydroxy succinimide [2,3] or (*S*)-3-hydroxy pyrrolidinyl ring [4] methacrylic esters bearing the azobenzene moiety linked to the ring nitrogen atom.

On the other hand, it is well known that photochromic polymers characterized by the presence of a strongly conjugated donor–acceptor system are widely investigated for reversible optical storage devices, non-linear optical applications and optoelectronics [5–8] and it appeared of interest to synthesize and investigate polymeric systems containing both photoresponsive azoaromatic chromophores with conjugated electron-donating and accepting groups, and optically active chiral groups capable to give rise to dissymmetric conformations of the macromolecules which could potentially provide non-centrosymmetric structures in the solid state, as required for obtaining second order optical non-linearity, particularly in thin films and surfaces [9]. With this aim, we report in the present paper the synthesis of the optically active monomers (*S*)-3-methacryloyloxy-1-(4′-cyano-4-azobenzene) pyrrolidine [(*S*)-**MAP-C**], (*S*)-3-methacryloyloxy-1-(4′-formyl-4-azobenzene) pyrrolidine [(*S*)-**MAP-F**], (*S*)-3-methacryloyloxy-1-[4′-(β-cyano-β-(methylsulfonyl)vinyl)-4-azobenzene] pyrrolidine [(*S*)-**MAP-S**] and (*S*)-3-methacryloyloxy-1-[4′-(β,β-dicyanovinyl)-4-azobenzene] pyrrolidine [(*S*)-**MAP-D**], their

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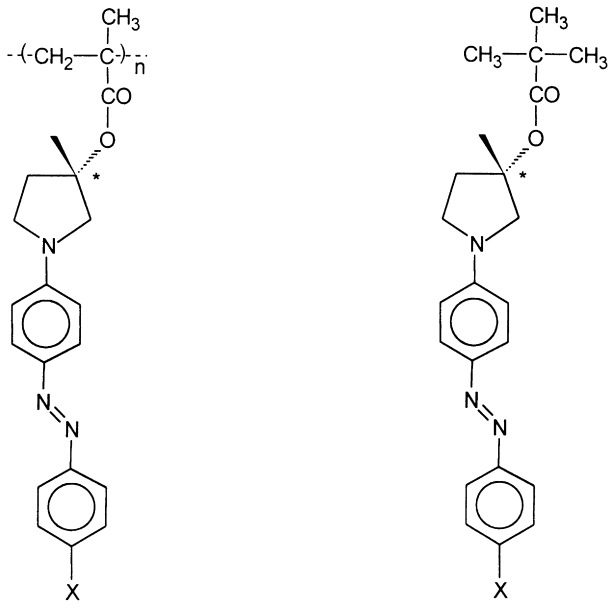


poly[(*S*)-**MAP-C**] [X = CN] (*S*)-**PAP-C**
poly[(*S*)-**MAP-F**] [X = CHO] (*S*)-**PAP-F**
poly[(*S*)-**MAP-S**] [X = CH=C(CN)(SO_2CH_3)] (*S*)-**PAP-S**
poly[(*S*)-**MAP-D**] [X = CH=C(CN)$_2$] (*S*)-**PAP-D**

Chart 1.

radical polymerization to the corresponding homopolymers poly[(*S*)-**MAP-X**], as well as the synthesis of the pivaloyl derivatives (*S*)-**PAP-X**, prepared as low molecular weight model compounds reproducing the structural repeating unit of the polymers, with the aim to evaluate the effect of the macromolecular structure on the physico-chemical properties of these substrates (Chart 1). The polymeric derivatives have been fully characterized and their spectroscopical properties compared to those of the corresponding models.

2. Experimental

2.1. Solvents and chemicals

Methacryloyl chloride (Aldrich) was distilled (bp 95°C) under inert atmosphere in the presence of traces of 2,6-di-*tert.*butyl-*p*-cresol as polymerization inhibitor before use. Pivaloyl chloride was distilled (bp 105–106°C) under inert atmosphere before use. Chloroform, tetrahydrofuran (THF), dimethylformamide (DMF), dimethylsulfoxide (DMSO), nitrobenzene and dimethylacetamide (DMA) were purified and dried according to reported procedures [10] and stored over molecular sieves (4 Å) under nitrogen. Triethylamine (Aldrich) was refluxed over dry $CaCl_2$ for 8 h, then distilled (bp 89°C) under nitrogen atmosphere. Azobisisobutyronitrile (AIBN) (Aldrich) was crystallized from abs. ethanol before use. All other reagents and solvents were used as received.

2.2. Synthesis of monomers and models

The previously reported procedure [4] adopted for the preparation of (*S*)-3-hydroxy-1-(4-azobenzene) pyrrolidine was followed for the synthesis of intermediates (*S*)-**2** and (*S*)-**3** starting from (*S*)-3-hydroxy-1-phenyl pyrrolidine [(*S*)-**1**] and, respectively, the diazonium salt of 4-cyano aniline (Aldrich) or 4-amino benzaldehyde, this latter obtained from 4-nitro toluene (Aldrich) by reaction with sodium sulphide and sulphur [11], according to a coupling procedure reported for similar derivatives [12].

(*S*)-3-Hydroxy-1-(4′-cyano-4-azobenzene) pyrrolidine [(*S*)-**2**] was obtained in 86% yield, mp 226–7°C.

^{1}H NMR: 7.95 and 7.85 (2d, 4H, arom. 3-H and 2′-H), 7.75 (d, 2H, arom. *ortho* to cyano group), 6.60 (d, 2H, arom. *ortho* to amino group), 4.75 (d, 1H, OH), 4.60 (m, 1H, 3-CH), 3.70–3.35 (m, 4H, 2- and 5-CH_2), 2.15 (m, 2H, 4-CH_2).

FT-IR: 3484 (ν_{OH}), 3080 (ν_{CH}, arom.), 2921 (ν_{CH}, aliph.), 2224 (ν_{CN}), 1603 and 1515 ($\nu_{C=C}$, arom.), 851 (δ_{CH}, 1,4-disubst. arom. ring), 824 (δ_{CH}, 1,4-disubst. arom. ring) cm^{-1}.

UV-VIS in THF: $\epsilon_{max} \times 10^{-3} = 35.3$ (458 nm) and 16.1 (278 nm) l mol^{-1} cm^{-1}.

(*S*)-3-Hydroxy-1-(4′-formyl-4-azobenzene) pyrrolidine [(*S*)-**3**] was obtained in 94% yield, mp 213–4°C.

^{1}H NMR: 10.05 (s, 1H, –CHO), 8.05–7.85 (3d, 6H, arom. *ortho* to formyl group and 2′-H and 3-H), 6.65 (d, 2H, arom. *ortho* to amino group), 4.60 (m, 1H, 3-CH), 4.50 (d, 1H, OH), 3.70–3.40 (m, 4H, 2- and 5-CH_2), 2.15 (m, 2H, 4-CH_2).

FT-IR: 3435 (ν_{OH}), 3068 (ν_{CH}, arom.), 2925 (ν_{CH}, aliph.), 1679 (ν_{CHO}), 1606 and 1518 ($\nu_{C=C}$, arom.), 845 (δ_{CH}, 1,4-disubst. arom. ring), 825 (δ_{CH}, 1,4-disubst. arom. ring) cm^{-1}.

UV–VIS in THF: $\epsilon_{max} \times 10^{-3} = 37.9$ (460 nm) and 13.6 (282 nm) l mol^{-1} cm^{-1}.

(*S*)-3-Methacryloyloxy-1-(4′-cyano-4-azobenzene) pyrrolidine [(*S*)-**MAP-C**] was prepared by reaction of methacryloyl chloride with (*S*)-**2** in the presence of dimethylamino pyridine (DMAP) as follows.

To an ice-cooled, vigorously stirred solution of (*S*)-**2** (2.50 g, 8.6 mmol), dimethylamino pyridine (0.10 g) as catalyst, and 2,6-di-*tert*-butyl-4-methyl phenol (0.10 g), as polymerization inhibitor, in dry methylene dichloride (52 ml), were simultaneously dropwise added, under nitrogen atmosphere, methacryloyl chloride (1.00 ml, 10.3 mmol) in methylene dichloride (5 ml) and triethylamine (1.44 ml, 10.3 mmol) in methylene dichloride (5 ml). The mixture was ice-cooled for 2 h, then left at room temperature for one night, washed with 0.1 M HCl, 5% Na_2CO_3 and finally with water, in that order. After drying the organic layer on anhydrous Na_2SO_4 and evaporation of the solvent under reduced pressure, the crude reaction product was purified by column chromatography (SiO_2, methylene dichloride as eluent) to afford pure (*S*)-**MAP-C** (66% yield), mp 120–2°C.

^{1}H NMR: 7.90 and 7.85 (2d, 4H, arom. 3-H and 2′-H), 7.55 (d, 2H, arom. *ortho* to cyano group), 6.65 (d, 2H, arom.

ortho to amino group), 6.10 and 5.60 (2d, 2H, CH_2=), 5.55 (m, 1H, 3-CH), 3.85–3.50 (m, 4H, 2- and 5-CH_2), 2.30 (m, 2H, 4-CH_2), 1.95 (s, 3H, CH_3).

FT-IR: 3011 (ν_{CH}, arom.), 2928 and 2860 (ν_{CH}, aliph.), 2219 (ν_{CN}), 1713 (ν_{CO}, ester), 1631 ($\nu_{C=C}$, methacrylic), 1605 and 1516 ($\nu_{C=C}$, arom.), 844 (δ_{CH}, 1,4-disubst. arom. ring), 825 (δ_{CH}, 1,4-disubst. arom. ring) cm^{-1}.

(*S*)-3-Pivaloyloxy-1-(4′-cyano-4-azobenzene) pyrrolidine [(*S*)-**PAP-C**] was similarly prepared from (*S*)-**2** (1.09 g, 3.74 mmol), dimethylamino pyridine (0.04 g), triethylamine (0.63 ml, 4.5 mmol) and pivaloyl chloride (0.55 ml, 4.50 mmol). The crude reaction product was purified by column chromatography (SiO_2, chloroform as eluent). Yield 54%, mp 138–9°C.

^{1}H NMR: 7.90 and 7.85 (2d, 4H, arom. 3-H and 2′-H), 7.70 (d, 2H, arom. *ortho* to cyano group), 6.60 (d, 2H, arom. *ortho* to amino group), 5.45 (m, 1H, 3-CH), 3.80–3.40 (m, 4H, 2- and 5-CH_2), 2.25 (m, 2H, 4-CH_2), 1.15 (s, 9H, CH_3).

FT-IR: 3083 (ν_{CH}, arom.), 2975 and 2871 (ν_{CH}, aliph.), 2220 (ν_{CN}), 1723 (ν_{CO}, ester), 1604 and 1516 ($\nu_{C=C}$, arom.), 849 (δ_{CH}, 1,4-disubst. arom. ring), 822 (δ_{CH}, 1,4-disubst. arom. ring), cm^{-1}.

A similar procedure to that one above described for (*S*)-**MAP-C** was followed for the preparation of (*S*)-3-methacryloyloxy-1-(4′-formyl-4-azobenzene) pyrrolidine [(*S*)-**MAP-F**], starting from (*S*)-**3** (6.60 g, 22.3 mmol), dimethylamino pyridine (0.26 g) and 2,6-di-*tert*-butyl-4-methyl phenol (0.16 g) in methylene dichloride (135 ml). The esterification reaction was performed by using methacryloyl chloride (2.61 ml, 26.8 mmol) and triethylamine (3.76 ml, 26.8 mmol). The pure monomeric compound was obtained by column chromatography (SiO_2, toluene/ethyl acetate 1:1 v/v as eluent). Yield 59%, mp 138–140°C.

^{1}H NMR: 10.05 (s, 1H, –CHO), 8.05–7.90 (3d, 6H, arom. *ortho* to cyano group and 2′-H and 3-H), 6.65 (d, 2H, arom. *ortho* to amino group), 6.10 and 5.60 (2d, 2H, CH_2=), 5.50 (m, 1H, 3-CH), 3.85–3.50 (m, 4H, 2- and 5-CH_2), 2.30 (m, 2H, 4-CH_2), 1.95 (s, 3H, CH_3).

FT-IR: 3071 (ν_{CH}, arom.), 2928 and 2848 (ν_{CH}, aliph.), 1703 (ν_{CO}, ester), 1679 (ν_{CHO}), 1631 ($\nu_{C=C}$, methacrylic), 1608 and 1516 ($\nu_{C=C}$, arom.), 836 (δ_{CH}, 1,4-disubst. arom. ring), 808 (δ_{CH}, 1,4-disubst. arom. ring) cm^{-1}.

(*S*)-3-Pivaloyloxy-1-(4′-formyl-4-azobenzene) pyrrolidine [(*S*)-**PAP-F**] was similarly prepared from (*S*)-**3** (3.20 g, 10.80 mmol), dimethylamino pyridine (0.05 g), triethylamine (1.81 ml, 13.0 mmol) and pivaloyl chloride (1.60 ml, 13.0 mmol). The crude reaction product was purified by column chromatography (SiO_2, toluene/ethyl acetate 5:1 v/v as eluent). Yield 47%. mp 157–8°C.

^{1}H NMR: 10.05 (s, 1H, –CHO), 8.00–7.85 (3d, 6H, arom. *ortho* to formyl group and 2′-H and 3-H), 6.60 (d, 2H, arom. *ortho* to amino group), 5.45 (m, 1H, 3-CH), 3.80–3.40 (m, 4H, 2- and 5-CH_2), 2.25 (m, 2H, 4-CH_2), 1.20 (s, 9H, CH_3).

FT-IR: 3079 (ν_{CH}, arom.), 2973 and 2851 (ν_{CH}, aliph.), 1724 (ν_{CO}, ester), 1686 (ν_{CHO}), 1607 and 1520 ($\nu_{C=C}$, arom.), 843 (δ_{CH}, 1,4-disubst. arom. ring), 815 (δ_{CH}, 1,4-disubst. arom. ring), cm^{-1}.

(*S*)-3-Hydroxy-1-[4′-(β-cyano-β-(methylsulfonyl)vinyl)-4-azobenzene] pyrrolidine [(*S*)-**4**].

The functionalization of (*S*)-**3** with (methylsulfonyl)acetonitrile was carried out following a procedure reported [13] for several azo-derivatives of similar structure. A mixture of (*S*)-**3** (2.00 g, 6.75 mmol), (methylsulfonyl)acetonitrile (0.81 g, 6.75 mmol) and ammonium acetate (0.53 g, 6.75 mmol) in 20.0 ml of absolute ethanol was stirred at reflux for 12 h under nitrogen, then cooled to room temperature. The precipitated product was filtered, washed with cold ethanol, and dried under vacuum to provide pure (*S*)-**4**. Yield 84%, mp not determined due to decomposition before melting.

^{1}H NMR (in DMSO-d_6): 8.45 (s, 1H, vinyl CH), 8.30 (d, 2H, arom. *ortho* to vinyl group), 8.05 and 7.95 (2d, 4H, arom. 3-H and 2′-H), 6.80 (d, 2H, arom. *ortho* to amino group), 5.20 (d, 1H, OH), 4.55 (m, 1H, 3-CH), 3.50 (s, 3H, SO_2CH_3), 3.70–3.35 (m, 4H, 2- and 5-CH_2), 2.20 (m, 2H, 4-CH_2).

FT-IR: 3327(ν_{OH}), 3028 (ν_{CH}, arom.), 2927 (ν_{CH}, aliph.), 2217 (ν_{CN}), 1604 and 1518 ($\nu_{C=C}$, arom.), 821 (δ_{CH}, 1,4-disubst. arom. rings) cm^{-1}.

UV-VIS in DMF: $\epsilon_{max} \times 10^{-3} = 37.9$ (510 nm) and 12.1 (321 nm) l mol^{-1} cm^{-1}.

(*S*)-3-Hydroxy-1-[4′-(2,2-dicyano-vinyl)-4-azobenzene] pyrrolidine [(*S*)-**5**] was similarly prepared from (*S*)-**3** (0.50 g, 1.70 mmol), malononitrile (0.11 g, 1.70 mmol) and ammonium acetate (0.13 g, 1.70 mmol) in 5.0 ml of absolute ethanol. Yield 77%, mp 203–204°C.

^{1}H NMR: 8.05 (d, 2H, arom. *ortho* to vinyl group), 7.95 and 7.90 (2d, 4H, arom. 3-H and 2′-H), 7.80 (s, 1H, vinyl CH), 6.65 (d, 2H, arom. *ortho* to amino group), 4.75 (d, 1H, OH), 4.60 (m, 1H, 3-CH), 3.65–3.45 (m, 4H, 2- and 5-CH_2), 2.15 (m, 2H, 4-CH_2).

FT-IR: 3489 (ν_{OH}), 3034 (ν_{CH}, arom.), 2909 (ν_{CH}, aliph.), 2226 (ν_{CN}), 1602 and 1521 ($\nu_{C=C}$, arom.), 836 (δ_{CH}, 1,4-disubst. arom. rings) cm^{-1}.

UV-VIS in DMA: $\epsilon_{max} \times 10^{-3} = 46.5$ (528 nm) and 14.5 (331 nm) l mol^{-1} cm^{-1}.

(*S*)-3-Methacryloyloxy-1-[4′-(β-cyano-β-(methylsulfonyl)-vinyl)-4-azobenzene] pyrrolidine [(*S*)-**MAP-S**] was prepared through two alternative routes in order to optimize the reaction yield as reported below in detail.

Route (a): To an ice-cooled, vigorously stirred solution in dry THF (350 ml) of (*S*)-**4** (3.90 g, 8.3 mmol), dimethylamino pyridine (0.11 g) as catalyst, and 2,6-di-*tert*-butyl-4-methyl phenol (0.10 g) as polymerization inhibitor, were simultaneously dropwise added, under nitrogen atmosphere, methacryloyl chloride (0.97 ml, 9.96 mmol) in THF (5 ml) and triethylamine (1.40 ml, 9.96 mmol) in THF (5 ml). The mixture was ice-cooled for 2 h, then left at room temperature for 36 h, concentrated at reduced pressure and the crude product dissolved in chloroform and filtered on to collect any unreacted (*S*)-**4**. The chloroformic solution was washed

with 0.1 M HCl, 5% Na_2CO_3 and finally with water, in that order. After drying the organic layer on anhydrous Na_2SO_4 and evaporation of the solvent under reduced pressure, the crude reaction product was purified by column chromatography (SiO_2, toluene/ethyl acetate 5:1 v/v as eluent) to afford pure (*S*)-**MAP-S**. Yield 26%.

Route (b): The monomeric compound (*S*)-**MAP-S** was obtained following a procedure based on the Knoevenagel condensation of (methylsulfonyl)acetonitrile on (*S*)-**MAP-F**. A mixture of (*S*)-**MAP-F** (3.00 g, 8.26 mmol), (methylsulfonyl)acetonitrile (1.02 g, 8.26 mmol), 2,6-di-*tert*-butyl-4-methyl phenol (0.10 g), as polymerization inhibitor, and ammonium acetate (0.64 g, 8.26 mmol) in 24.0 ml of absolute ethanol was stirred, under nitrogen, at reflux for 12 h, and the reaction progress followed by TLC on silica gel using toluene/ethyl acetate 5:1 v/v as eluent. At the end of the reaction the mixture was cooled to room temperature and the precipitated product filtered, washed with cold ethanol, and purified by column chromatography (SiO_2, toluene/ethyl acetate 5:1 v/v as eluent). Yield 73%, mp 215–6°C.

^{1}H NMR: 8.15 (s, 1H, vinyl CH), 8.10 (d, 2H, arom. *ortho* to vinyl group), 7.95 and 7.90 (2d, 4H, 3-H and 2′-H), 6.65 (d, 2H, arom. *ortho* to amino group), 6.15 and 5.60 (2d, 2H, CH_2═), 5.55 (m, 1H, 3-CH), 3.85–3.50 (m, 4H, 2- and 5-CH_2), 3.25 (s, 3H, SO_2CH_3), 2.30 (m, 2H, 4-CH_2), 1.95 (s, 3H, CH_3).

FT-IR: 3030 (ν_{CH}, arom.), 2924 and 2870 (ν_{CH}, aliph.), 2216 (ν_{CN}), 1709 (ν_{CO}, ester), 1631 ($\nu_{C=C}$, methacrylic), 1604 and 1518 ($\nu_{C=C}$, arom.), 822 (δ_{CH}, 1,4-disubst. arom. rings) cm^{-1}.

The model compound (*S*)-3-pivaloyloxy-1-[4′-(β-cyano-β-(methylsulfonyl)vinyl)-4-azobenzene] pyrrolidine [(*S*)-**PAP-S**] was prepared according to route (b) by Knoevenagel condensation of (*S*)-**PAP-F** (1.00 g, 2.63 mmol) with (methylsulfonyl)acetonitrile (0.31 g, 2.63 mmol) in absolute ethanol (24.0 ml) in the presence of ammonium acetate (0.20 g, 2.63 mmol). The crude product was purified by crystallization from absolute ethanol to provide pure (*S*)-**PAP-S**. Yield 61%, mp 173–5°C.

^{1}H NMR: 8.15 (s, 1H, vinyl CH), 8.05 (d, 2H, arom. *ortho* to vinyl group), 7.95 and 7.90 (2d, 4H, 3-H and 2′-H), 6.65 (d, 2H, arom. *ortho* to amino group), 5.45 (m, 1H, 3-CH), 3.80–3.40 (m, 4H, 2- and 5-CH_2), 3.15 (s, 3H, SO_2CH_3), 2.25 (m, 2H, 4-CH_2), 1.20 (s, 9H, CH_3).

FT-IR: 3072 (ν_{CH}, arom.), 2975 and 2868 (ν_{CH}, aliph.), 2211 (ν_{CN}), 1721 (ν_{CO}, ester), 1601 and 1517 ($\nu_{C=C}$, arom.), 843 (δ_{CH}, 1,4-disubst. arom. ring), 829 (δ_{CH}, 1,4-disubst. arom. ring) cm^{-1}.

(*S*)-3-Methacryloyloxy-1-[4′-(β,β-dicyano-vinyl)-4-azobenzene] pyrrolidine [(*S*)-**MAP-D**] was prepared according to route (b) by refluxing for 12 h a stirred mixture of (*S*)-**MAP-F** (1.50 g, 4.13 mmol), malononitrile (0.27 g, 4.13 mmol), 2,6-di-*tert*-butyl-4-methyl phenol (0.10 g), as polymerization inhibitor, and ammonium acetate (0.32 g, 4.13 mmol) in 12.0 ml of absolute ethanol, under nitrogen. The reaction progress was followed by TLC on silica gel using chloroform as eluent. The mixture was cooled to room temperature and the precipitated product filtered, washed with cold ethanol, and crystallized from absolute ethanol. Yield 89%, mp 179–181°C.

^{1}H NMR: 8.00 (d, 2H, arom. *ortho* to vinyl group), 7.95 and 7.90 (2d, 4H, arom. 3-H and 2′-H), 7.75 (s, 1H, vinyl CH), 6.65 (d, 2H, arom. *ortho* to amino group), 6.15 and 5.60 (2d, 2H, CH_2═), 5.55 (m, 1H, 3-CH), 3.80–3.60 (m, 4H, 2- and 5-CH_2), 2.35 (m, 2H, 4-CH_2), 1.95 (s, 3H, CH_3).

FT-IR: 3036 (ν_{CH}, arom.), 2963 and 2922 (ν_{CH}, aliph.), 2220 (ν_{CN}), 1717 (ν_{CO}, ester), 1631 ($\nu_{C=C}$, methacrylic), 1607 and 1582 ($\nu_{C=C}$, arom.), 835 (δ_{CH}, 1,4-disubst. arom. ring), 803 (δ_{CH}, 1,4-disubst. arom. ring) cm^{-1}.

(*S*)-3-Pivaloyloxy-1-[4′-(β,β-dicyano-vinyl)-4-azobenzene] pyrrolidine [(*S*)-**PAP-D**] was similarly prepared from (*S*)-**PAP-F** (0.70 g, 1.84 mmol), malononitrile (0.12 g, 1.84 mmol) and ammonium acetate (0.14 g, 1.84 mmol) in absolute ethanol (5.5 ml). The crude product was purified by crystallization from absolute ethanol. Yield 65%, mp 212–4°C.

^{1}H NMR: 8.00–7.85 (3d, 6H, arom. *ortho* to vinyl group and 3-H and 2′-H), 7.75 (s, 1H, vinyl CH), 6.65 (d, 2H, arom. *ortho* to amino group), 5.45 (m, 1H, 3-CH), 3.80–3.45 (m, 4H, 2- and 5-CH_2), 2.25 (m, 2H, 4-CH_2), 1.20 (s, 9H, CH_3).

FT-IR: 3077 (ν_{CH}, arom.), 2977 and 2861 (ν_{CH}, aliph.), 2226 (ν_{CN}), 1731 (ν_{CO}, ester), 1606 and 1520 ($\nu_{C=C}$, arom.), 836 (δ_{CH}, 1,4-disubst. arom. ring), 826 (δ_{CH}, 1,4-disubst. arom. ring) cm^{-1}.

2.3. Polymerization of monomers

All polymerization reactions were carried out in glass vials using AIBN as free radical thermal initiator (2% w/w with respect to monomer) in dry THF solutions (15 ml) containing 1 g of monomer, with the exception of (*S*)-**MAP-S**, which was polymerized in dry DMF (1 g of monomer in 25 ml) [13]. The reaction mixture was introduced into the vial under nitrogen atmosphere, submitted to several freeze-thaw cycles in order to eliminate any trace of dissolved oxygen, and heated at 60°C for 72 h. The crude product was precipitated from solution by pouring the reaction mixture into a large excess of methanol (100 ml) and collected by filtration. The solid material was then repeatedly dissolved in DMF and reprecipitated in methanol. The last traces of unreacted monomer were eliminated from the product by Soxhlet extraction with methanol followed by acetone (methanol only was used for the polymer deriving from (*S*)-**MAP-S**). The purified products were finally thoroughly dried to constant weight under vacuum at 80°C for 4 days. The dried polymers were hardly soluble in THF or $CHCl_3$ and required the addition of small amounts of a strongly polar solvent, such as nitrobenzene, DMF, DMA or DMSO in order to achieve a satisfactory solubility for the

Table 1
Characterization data of the polymers

Polymer	Yield (%)[a]	$\bar{M}_n$ (g/mol)[b]	$\bar{M}_w/\bar{M}_n$[b]	T_d (°C)[c]	T_g (°C)[d]
Poly[(*S*)-**MAP-C**]	49	43 900	1.4	311	192
Poly[(*S*)-**MAP-F**]	61	41 000	1.6	309	187
Poly[(*S*)-**MAP-S**]	66	37 600	1.4	297	196
Poly[(*S*)-**MAP-D**]	54	30 000	1.6	290	198

[a] Calculated as (g polymer/g monomer) 100.
[b] Determined by GPC in THF at 25°C.
[c] Determined by TGA.
[d] Determined by DSC.

determinations in solution. Relevant data for the synthesized products are reported in Table 1.

*Poly[(S)-**MAP-C**]*. ^{1}H NMR (in DMSO-d_6 at 100°C): 7.95–7.60 (m, 6H, arom. 3-H and 2′-H and 3′-H), 6.50 (m, 2H, arom. *ortho* to amino group), 5.20–4.95 (m, 1H, 3-CH), 3.70–3.10 (m, 4H, 2- and 5-CH_2), 2.30–1.10 (m, 4H, 4-CH_2 and backbone CH_2), 1.10–0.60 (m, 3H, CH_3).

^{13}C NMR (in nitrobenzene-d_5): 179.0–176.0 (CO), 155.4 (arom. *C*–CN), 150.7, 148.4, 144.1 (arom. *C*–N═N–*C* and *C*–NCH_2), 132.9 (arom. 3′-C), 125.9, 123.5 (arom. 2′-C and 3-C), 118.7 (CN), 111.9 (arom. 2-C), 74.8 (CH–O), 55.5 (main chain *C*H_2–C), 52.6 (CH–*C*H_2–N), 47.4 (CH_2–*C*H_2–N), 46.0 (main chain CH_2–*C*), 30.7 (CH–*C*H_2–CH_2), 19.7 and 17.9 (CH_3).

FT-IR: 3052 (ν_{CH}, arom.), 2943, 2856 (ν_{CH}, aliph.), 2224 (ν_{CN}), 1728 (ν_{CO}, ester), 1597 and 1516 ($\nu_{C=C}$, arom.), 1136 (ν_{C-O}), 846 (δ_{CH}, 1,4-disubst. arom. ring), 822 (δ_{CH}, 1,4-disubst. arom. ring) cm^{-1}.

*Poly[(S)-**MAP-F**]*. ^{1}H NMR (in DMSO-d_6 at 100°C): 9.95 (s, 1H, CHO), 8.00–7.55 (m, 6H, arom. 3-H and 2′-H and 3′-H), 6.50 (m, 2H, arom. *ortho* to amino group), 5.30–4.90 (m, 1H, 3-CH), 3.70–3.00 (m, 4H, 2- and 5-CH_2), 2.30–1.10 (m, 4H, 4-CH_2 and backbone CH_2), 1.10–0.55 (m, 3H, CH_3).

^{13}C NMR (in nitrobenzene-d_5): 191.5 (CHO), 178.0–175.6 (CO), 156.9 (arom. *C*–CHO), 150.6, 144.3, 136.8 (arom. *C*–N═N–*C* and *C*–NCH_2), 131.0 (arom. 3′-C), 126.3, 123.0 (arom. 2′-C and 3-C), 112.2 (arom. 2-C), 75.2 (CH–O), 55.0 (main chain *C*H_2–C), 52.9 (CH–*C*H_2–N), 46.3 (CH_2–*C*H_2–N), 45.7 (main chain CH_2–*C*), 31.1 (CH–*C*H_2–CH_2), 19.8 and 18.0 (CH_3).

FT-IR: 3052 (ν_{CH}, arom.), 2981, 2854 (ν_{CH}, aliph.), 1727 (ν_{CO}, ester), 1697 (ν_{CHO}), 1595 and 1516 ($\nu_{C=C}$, arom.), 1133 (ν_{C-O}), 841 (δ_{CH}, 1,4-disubst. arom. ring), 823 (δ_{CH}, 1,4-disubst. arom. ring) cm^{-1}.

*Poly[(S)-**MAP-S**]*. ^{1}H NMR (in DMSO-d_6 at 100°C): 8.20 (s, 1H, vinyl CH), 8.05 (m, 2H, arom. *ortho* to vinyl group), 7.90–7.60 (m, 4H, arom. 3-H and 2′-H), 6.55 (m, 2H, arom. *ortho* to amino group), 5.20–4.90 (m, 1H, 3-CH), 3.80–3.10 (m, 7H, SO_2CH_3 and 2- and 5-CH_2), 2.40–1.10 (m, 4H, 4-CH_2 and backbone CH_2), 1.05–0.60 (m, 3H, CH_3).

^{13}C NMR (in nitrobenzene-d_5): 178.5–176.0 (CO), 156.9 (arom. *C*–CH═), 152.3 (CH═), 151.3, 148.8, 145.0 (arom. *C*–N═N–*C* and *C*–NCH_2), 132.6 (arom. 3′-C), 131.1 (*C*(CN)(SO_2CH_3)), 126.6, 123.5 (arom. 2′-C and 3-C), 114.1 (CN), 112.5 (arom. 2-C), 75.3 (CH–O), 55.6 (main chain *C*H_2–C), 53.3 (CH–*C*H_2–N), 46.6 (CH_2–*C*H_2–N), 46.3 (main chain CH_2–*C*), 42.3 (SO_2CH_3), 31.3 (CH–*C*H_2–CH_2), 20.5 and 18.7 (CH_3).

FT-IR: 3072 (ν_{CH}, arom.), 2925, 2857 (ν_{CH}, aliph.), 2213 (ν_{CN}), 1728 (ν_{CO}, ester), 1602 and 1516 ($\nu_{C=C}$, arom.), 1132 (ν_{C-O}), 843 (δ_{CH}, 1,4-disubst. arom. ring), 823 (δ_{CH}, 1,4-disubst. arom. ring) cm^{-1}.

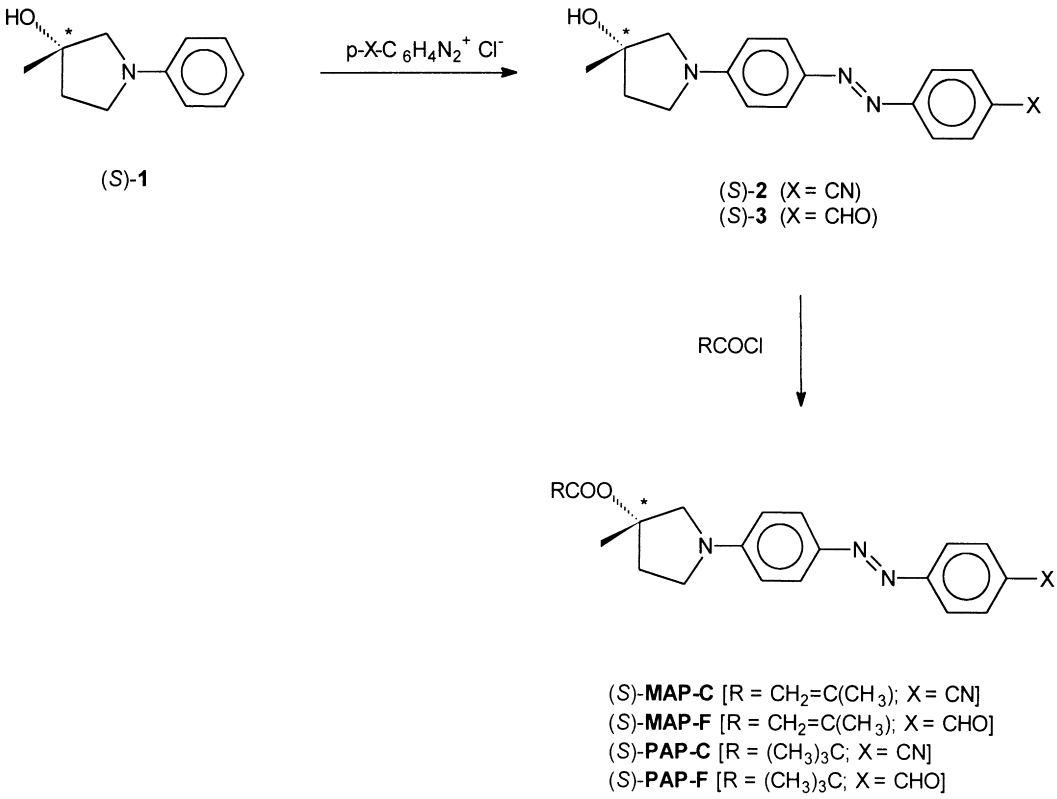
*Poly[(S)-**MAP-D**]*. ^{1}H NMR (in DMSO-d_6 at 100°C): 8.20 (s, 1H, vinyl CH), 8.10–7.40 (m, 6H, arom. 3-H and 2′-H and 3′-H), 6.50 (m, 2H, arom. *ortho* to amino group), 5.30–4.90 (m, 1H, 3-CH), 3.80–3.10 (m, 4H, 2- and 5-CH_2), 2.30–1.10 (m, 4H, 4-CH_2 and backbone CH_2), 1.10–0.60 (m, 3H, CH_3).

^{13}C NMR (in nitrobenzene-d_5): 179.0–176.0 (CO), 159.5 (arom. *C*–CH═), 157.3 (CH═), 151.7, 149.1, 145.3 (arom. *C*–N═N–*C* and *C*–NCH_2), 132.7 (arom. 3′-C), 132.3 (*C*$(CN)_2$), 127.0, 123.5 (arom. 2′-C and 3-C), 114.9 and 114.0 (CN), 112.9 (arom. 2-C), 75.7 (CH–O), 55.5 (main chain *C*H_2–C), 53.6 (CH–*C*H_2–N), 47.0 (CH_2–*C*H_2–N), 46.2 (main chain CH_2–*C*), 31.6 (CH–*C*H_2–CH_2), 20.7 and 19.1 (CH_3).

FT-IR: 3077 (ν_{CH}, arom.), 2925, 2846 (ν_{CH}, aliph.), 2225 (ν_{CN}), 1727 (ν_{CO}, ester), 1603 and 1515 ($\nu_{C=C}$, arom.), 1131 (ν_{C-O}), 839 (δ_{CH}, 1,4-disubst. arom. ring), 821 (δ_{CH}, 1,4-disubst. arom. ring) cm^{-1}.

2.4. Physicochemical measurements

NMR spectra were recorded at room temperature on 5–10% $CDCl_3$ solutions, unless otherwise stated, using a Varian NMR Gemini 300 spectrometer. Chem. shifts are given in ppm from tetramethylsilane (TMS) as internal reference. ^{1}H NMR spectra were performed at 300 MHz by using the following experimental conditions: 24000



Scheme 1.

data points, 4.5 kHz spectral width, 2.6 s acquisition time, 16 transients. ^{13}C NMR spectra were recorded at 75.5 MHz, under full proton decoupling, by using the following experimental conditions: 24000 data points, 20 kHz spectral width, 0.6 s acquisition time, 64000 transients. Microtacticity evaluation of polymeric derivatives was based on the peak areas ratio of the methyl resonances at ca. 20 and 18–19 ppm, related to *mr* and *rr* triads [14], respectively, which allows to obtain the probability of formation of a *m* dyad P_m and of a *r* dyad $P_r = 1 - P_m$, from the expression $2P_m(1 - P_m)/(1 - P_m)^2$, corresponding to the ratio between the amounts of *mr* and *rr* triads. The probability *P* that a certain dyad is linked to another dyad of the same or the opposite relative configuration was calculated from the expressions: $P_{m/m} = mm/m$, $P_{r/m} = mr/2m$, $P_{r/r} = rr/r$ and $P_{m/r} = mr/2r$, where *m*, *r*, *mm*, *rr*, and *mr* are the amounts of the corresponding dyads and triads as determined by the spectra.

FT-IR spectra were carried out on a Perkin–Elmer 1750 spectrophotometer, equipped with an Epson Endeavour II data station, on samples prepared as KBr pellets.

UV-VIS absorption spectra were recorded at 25°C in the 650–250 nm spectral region with a Perkin–Elmer Lambda 19 spectrophotometer on $CHCl_3$, THF, DMF or DMA solutions by using cell path lengths of 0.1 cm. Concentrations in azobenzene chromophore of about 8×10^{-4} mol l^{-1} were used.

CD spectra were recorded at 25°C on a Jasco 500 A dichrograph, using the same pathlengths and solution concentrations as for UV measurements. $\Delta\epsilon$ values, expressed as l mol^{-1} cm^{-1}, were calculated by the following equation: $\Delta\epsilon = [\Theta]/3300$, where the molar ellipticity $[\Theta]$ in deg cm^2 $dmol^{-1}$ refers to one azobenzene chromophore.

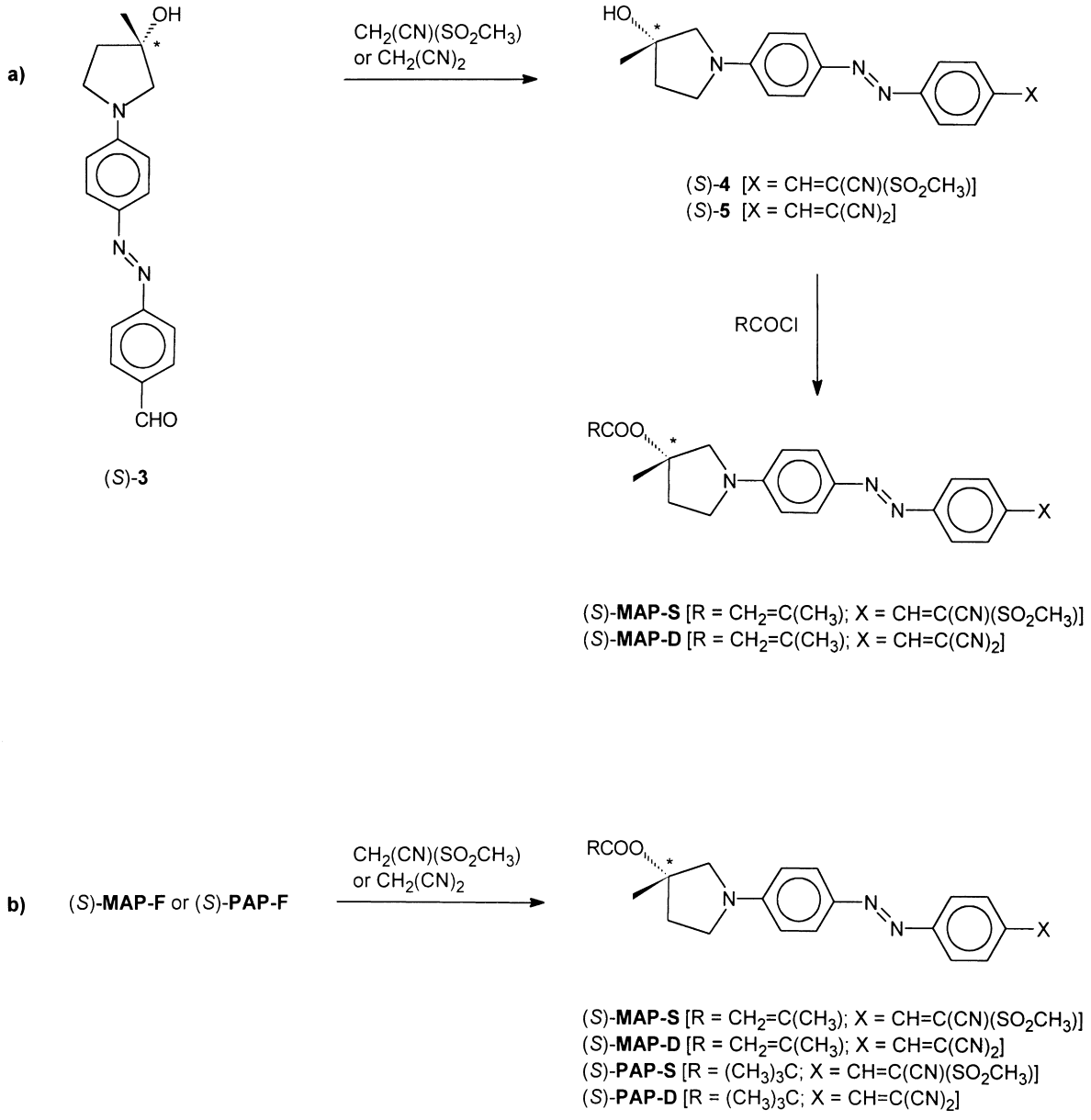
Number average molecular weights of the polymers ($\bar{M}_n$) were determined in THF or DMA solution by SEC using a HPLC Lab Flow 2000 apparatus, equipped with an injector Rheodyne 7725i, a Phenomenex Phenogel 5 micron MXL column and an UV-VIS detector Linear Instruments model UVIS-200, working at 254 nm. Calibration curves were obtained by using several monodisperse polystyrene standards.

The glass transition temperature values of polymers (T_g) were measured by differential scanning calorimetry (DSC) on a TA Instruments DSC 2920 Modulated apparatus at a heating rate of 10°C/min under nitrogen atmosphere. Each sample was heated up to only 250°C in order to avoid thermal decomposition. The initial thermal decomposition temperature (T_d) was determined on the polymer samples with a Perkin–Elmer TGA-7 thermogravimetric analyzer by heating the samples in air at a rate of 20°K/min. Melting points (uncorrected) were determined in glass capillaries on a Büchi 510 apparatus at a heating rate of 1°C/min.

3. Results and discussion

3.1. Synthesis

The synthesis of monomers (*S*)-**MAP-C** and (*S*)-**MAP-F** was carried out starting from (*S*)-3-hydroxy-1-phenyl



Scheme 2.

pyrrolidine (*S*)-**1** [4] (Scheme 1) through coupling with the appropriate diazonium salt deriving from 4-cyano aniline or 4-amino benzaldehyde to give, respectively, (*S*)-3-hydroxy-1-(4′-cyano-4-azobenzene) pyrrolidine (*S*)-**2** and (*S*)-3-hydroxy-1-(4′-formyl-4-azobenzene) pyrrolidine (*S*)-**3**. Alcohols **2** and **3** were then allowed to react with methacryloyl chloride or pivaloyl chloride, thus affording monomers (*S*)-**MAP-C** and (*S*)-**MAP-F**, as well as the model compounds (*S*)-**PAP-C** and (*S*)-**PAP-F**.

Monomer (*S*)-**MAP-S** was prepared through two alternative routes (Scheme 2), starting both from alcohol (*S*)-**3**, in order to optimize the reaction yield. The first one [route (a)] consisted in the preliminary functionalization of (*S*)-**3** with (methylsulfonyl)acetonitrile to (*S*)-3-hydroxy-1-[4′-(β-cyano-β-(methylsulfonyl)vinyl)-4-azobenzene] pyrrolidine (*S*)-**4**, followed by reaction with methacryloyl chloride to give (*S*)-**MAP-S** in low yield (26%), mainly in consequence of the low solubility of (*S*)-**4** in the reaction solvent (THF or dichloromethane). The second route (b), involving a procedure based on the Knoevenagel condensation of (methylsulfonyl)acetonitrile on (*S*)-**MAP-F**, prepared as reported in Scheme 1, resulted more convenient, with an improved overall yield in (*S*)-**MAP-S** of 43%, including the reaction yield of the synthesis of (*S*)-**MAP-F** from (*S*)-**3**, as compared to the 22% of the former one. Accordingly, model (*S*)-**PAP-S** was also synthesized by the Knoevenagel reaction on (*S*)-**PAP-F**. Monomer (*S*)-**MAP-D** and model (*S*)-**PAP-D** (Scheme 2) were similarly prepared

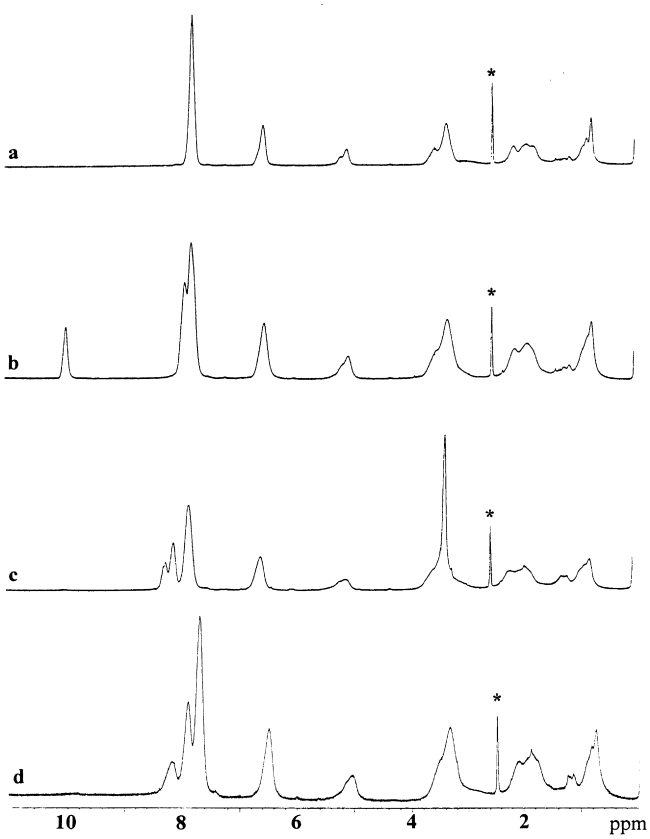


Fig. 1. ^{1}H NMR spectra of poly[(*S*)-**MAP-C**] (a), poly[(*S*)-**MAP-F**] (b), poly[(*S*)-**MAP-S**] (c) and poly[(*S*)-**MAP-D**] (d) in DMSO-d_6 at 100°C. Starred signals refer to solvent resonances.

from (*S*)-**MAP-F** and (*S*)-**PAP-F**, respectively, by reaction with malononitrile, having verified the insufficient solubility of the intermediate (*S*)-3-hydroxy-1-[4′-(β,β-dicyanovinyl)-4-azobenzene] pyrrolidine (*S*)-**5** in the acylation medium of the reaction with methacryloyl or pivaloyl chloride.

The structures of all monomers and models were confirmed by ^{1}H NMR and FT-IR (see Experimental). The optical activity at the sodium D-line of monomers and models, as well as that of intermediates **2**-**5**, could not be measured with accuracy due to the strong absorption of the azoaromatic chromophore at that wavelength. However, previous data concerning the optical purity of the 4′-unsubstituted methacryloyl and pivaloyl derivatives prepared through a similar synthetic pathway [4] indicated that an enantiomeric excess of at least the 90% was present in those compounds, thus excluding the possibility of racemization of the chiral center in the course of the synthesis. This allows to reasonably attribute an analogous optical purity also to the monomers and models reported in the present paper.

3.2. Polymers characterization

Polymerization of the monomers, carried out in solution under radical conditions by using AIBN as a thermal initiator, produced the corresponding polymeric derivatives in acceptable yields after purification (Table 1), with average molecular weight and polydispersity values, as determined by gel permeation chromatography, in the range expected for this type of process. The FT-IR spectra of the polymers confirmed the occurrence of polymerization involving the methacrylic double bond, with the disappearance of the band around 1634 cm^{-1} (stretching vibration of the aliphatic double bond of the monomer) and the presence of a new absorption band related to the α,β saturated ester group at 1728–1731 cm^{-1}, in the same spectral region as the model compounds, with a shift of 10–20 cm^{-1} to higher frequencies with respect to the stretching carbonyl frequency present in the corresponding monomer. In accordance with FT-IR data, the resonances at 5.60 and 6.15 ppm, related to the methacrylic CH_2 protons, were absent in the ^{1}H NMR spectra of the polymers (Fig. 1), and the resonance of the methacrylic CH_3 was shifted from 1.95 ppm in the monomer to 0.60 ppm in the corresponding polymer.

The thermal stability of the products (Table 1), as determined by TGA, appears rather high, with values of initial decomposition in air ranging around 300°C, indicative of the occurrence of strong inter- and intramolecular dipolar interactions originated by presence of high charge delocalization in the macromolecular side chains. By comparison, the corresponding decomposition temperature for poly(methyl

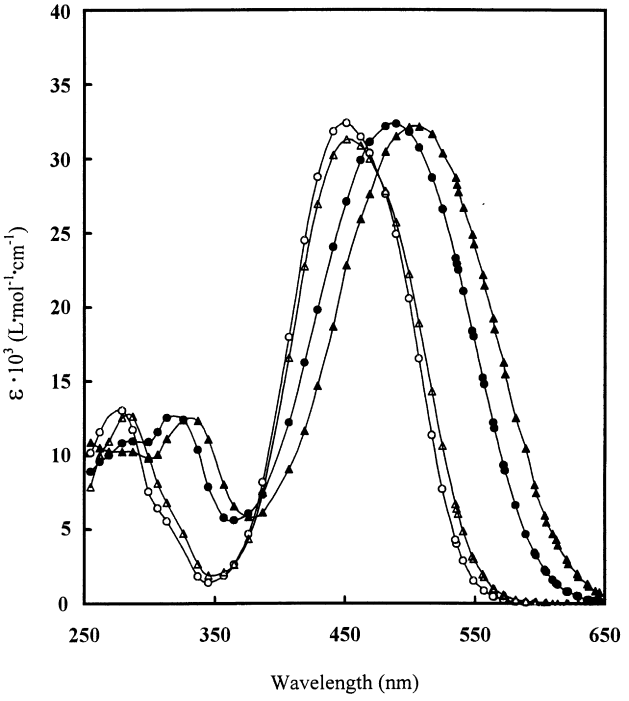


Fig. 2. UV spectra in DMA of poly[(*S*)-**MAP-C**] (-○-), poly[(*S*)-**MAP-F**] (-△-), poly[(*S*)-**MAP-S**] (-●-) and poly[(*S*)-**MAP-D**] (-▲-).

methacrylate) is reported at 260°C [15]. Only endothermic glass transitions, with no melting peaks, are observed in the DSC traces, in agreement with a substantially amorphous structure of these materials. In accordance with a reduced mobility of the macromolecular chains originated by their dipolar structure and conformational stiffness, it can be noted that the T_g values, ranging around 200°C, are remarkably higher than those reported for the 4′-unsubstituted polymer (169°C) [4], lacking of a strong electron acceptor group in the conjugated azoaromatic system, as well as for the methacrylic polymer **PDR1M** (129°C) [16], containing in the side chain the flexible chromophore 4′-[(2-hydroxyethyl)ethylamino]-4-nitroazobenzene (Disperse Red 1), and even for a polyacrylamide bearing in the side chain the more rigid *N*-4-(4-nitrophenylazo)phenyl piperazine chromophore (156°C) [17].

The UV spectra in DMA solution of polymers and models (Fig. 2) display two absorption bands centered in the 450–510 and 280–330 nm spectral regions, the former, more intense, related to the combined contributions of the n–π^*, first π–π^* and internal charge transfer electronic transitions of the azobenzene chromophore, and the latter to the π–π^* electronic transition of the aromatic ring [18]. A significantly increasing bathochromic effect can be noted in both bands of polymeric and model derivatives on passing from X = CN to CHO, CH═C(SO_2CH_3)(CN), CH═C($CN)_2$ (Table 2), as a consequence of the increasing electron-withdrawing capability of the substituent and hence of the conjugation extent in the aromatic chromophore [19], giving rise to a progressive reduction of the electronic transition energy in the system. It can be

Table 2
UV spectra in DMA of polymers and model compounds

	1st Band		2nd Band	
Sample	λ_{max} [a]	$\epsilon_{max} \times 0^{-3}$ [b]	λ_{max} [a]	$\epsilon_{max} \times 10^{-3}$ [b]
Poly[(*S*)-**MAP-C**]	447	32.4	277	12.4
(*S*)-**PAP-C**	458	35.4	277	12.4
Poly[(*S*)-**MAP-F**]	454	31.3	283	12.0
(*S*)-**PAP-F**	464	33.0	283	12.1
Poly[(*S*)-**MAP-S**]	486	32.3	318	12.3
(*S*)-**PAP-S**	500	36.6	323	12.6
Poly[(*S*)-**MAP-D**]	503	32.2	331	12.2
(*S*)-**PAP-D**	516	41.6	330	13.5

[a] Wavelength of maximum absorbance, expressed in nm.
[b] Expressed in l mol^{-1} cm^{-1} and calculated for one repeating unit in the polymers.

therefore deduced that the dicyanovinyl substituent in 4′ position of the azoaromatic moiety provides the highest charge delocalization in the investigated systems. Indeed, this group is reported to display a higher acceptor strength than the formyl and even the nitro group [20,21] in analogous donor-acceptor conjugated systems.

A relevant hypochromism, more evident in the 1st band, particularly in the systems displaying a higher conjugation extent in the chromophore, can be observed when the spectra of model compounds are compared with those of the corresponding polymers (Table 2). This effect, frequently noticed in polymeric derivatives bearing side-chain aromatic chromophores [3,4,22–24], is attributed to the presence of electrostatic dipolar interactions between neighboring aromatic chromophores [25–27], and appears indeed significantly maximized ($\epsilon_{model} - \epsilon_{polymer} = 9.4 \times 10^3$ l mol^{-1} cm^{-1}) for the (*S*)-**PAP-D**/poly[(*S*)-**MAP-D**] couple, possessing the highest permanent dipole moment of the series. A systematic shift ($\Delta\lambda$ 10–14 nm) to shorter wavelength of the maximum absorption of the first band can also be observed on passing from the model to the corresponding homopolymer (Table 2). A similar effect, with a blue shift of 15 nm in DMSO solution, was also observed for the above cited methacrylic polymer **PDR1M** in comparison with the monomer [28], and attributed to intramolecular anti-parallel interaction of the adjacent side-chain dipoles, this arrangement being probably favorably affected by the prevalent syndiotacticity of the macromolecules [29]. The occurrence in azobenzene-containing ammonium amphiphiles in water dispersion of a blue shift of the UV absorption band with respect to the maximum wavelength displayed by the chromophores in the disordered state, is reported to indicate a parallel stacking of the chromophores (H-aggregates), a red shift being vice-versa indicative of head-to-tail orientation (J-aggregates) [30,31]. Accordingly, a parallel arrangement of chromophores (H-aggregates) has been proposed on the basis of the presence of a blue shift of the UV maximum, as compared to the solution, in the spectra of Langmuir–Blodgett (LB) mono- and multi-layers

Table 3
CD spectra in DMA of polymers and model compounds

Sample	1st Band				2nd Band			
	λ_1[a]	$\Delta\epsilon_1$[b]	λ_2[a]	$\Delta\epsilon_2$[b]	λ_3[a]	$\Delta\epsilon_3$[b]	λ_4[a]	$\Delta\epsilon_4$[b]
Poly[(*S*)-**MAP-C**]	491	+10.24	421	−7.35	291	+0.40	263	−0.36
(*S*)-**PAP-C**	460	+0.64	–	–	277	−0.23	–	–
Poly[(*S*)-**MAP-F**]	495	+8.58	418	−6.30	298	+0.43	277	−0.37
(*S*)-**PAP-F**	465	+0.50	–	–	281	−0.25	–	–
Poly[(*S*)-**MAP-S**]	537	+9.06	446	−5.28	337	+0.33	307	−0.40
(*S*)-**PAP-S**	502	+0.60	–	–	325	−0.30	–	–
Poly[(*S*)-**MAP-D**]	548	+8.91	445	−4.70	345	+0.50	318	−0.62
(*S*)-**PAP-D**	518	+0.57	–	–	331	−0.34	–	–

[a] Wavelength of maximum dichroic absorption, expressed in nm.
[b] Expressed in l mol^{-1} cm^{-1} and calculated for one repeating unit in the polymers.

of mixtures of amylose acetate and a chiral *p*-nitro azobis-[benzene] dye containing the (*R*)-3-hydroxypyrrolidine ring [32,33], as well as of LB polymeric films of optically active poly(L-glutamate)s bearing side-chain azobenzene moieties tethered by alkyl spacers of different length [34]. Conversely, a red shift of the $\pi-\pi^*$ transition band with respect to the solution spectra, indicative of an anti-parallel type aggregation (J-aggregation) of the chromophores was observed in the UV spectra of achiral polymethacrylate bearing in the side chain the azoaromatic dye Disperse Red 13 in Langmuir and LB films of the pure homopolymer [35] and of mixtures of the homopolymer with Cd stearate [36]. Similarly, LB mixed films of Disperse Red 19 isophorone polyurethane and Cd stearate displayed a red shift of the UV maximum when compared to the solution spectrum [37].

Assuming that no aggregates are present in the monomeric models in solution and that the $\pi-\pi^*$ band is the same for the polymer and the corresponding model, though the chromophores are anchored to the polymer backbone [34], it therefore appears that a parallel type aggregation of chromophores, presumably of intramolecular nature, is present to some extent also in poly[(*S*)-**MAP-X**] substrates in solution, evidently as a consequence of the close proximity to each other of the side chain chromophores located along the macromolecular backbone, thus favoring the possibility of their mutual interaction. Taking into account that in poly[(*S*)-**MAP-X**]s the observed hypsochromism is slightly enhanced by the increase of the electron withdrawing ability of substituent X, and hence by the dipole moment value of the chromophores (Table 2), one can deduce that this H-type aggregation is originated by the structural constraints of the macromolecules which are able to counterbalance the electrostatic repulsions expected in dipoles facing each other with approximately the same orientation.

By contrast with the models, exhibiting only a weak positive or negative signal (Table 3) in correspondence of the UV absorptions related to the 1st and the 2nd bands, the CD spectra in DMA solution of the polymers (Table 3 and Fig. 3) display two strong signals of opposite sign in the spectral region connected to the 1st UV band, with a cross-over point in correspondence of the UV maximum absorption, thus evidencing the same bathochromism related to the above mentioned substituent effect. Such a behavior, observed also in analogous optically active methacrylic polymers with pendant azoaromatic moieties lacking of the electron acceptor substituent in the $4'$ position [3,4], is typical of exciton splitting originated by cooperative interactions between side-chain azoaromatic chromophores disposed in a mutual chiral geometry of one prevailing handedness [38]. Accordingly, model compounds, which are randomly distributed in solution, do not exhibit any significant optical activity. The enhancement of conjugation afforded by the presence of a strong donor-acceptor system, as observed also when X in poly[(*S*)-**MAP-X**] is the nitro

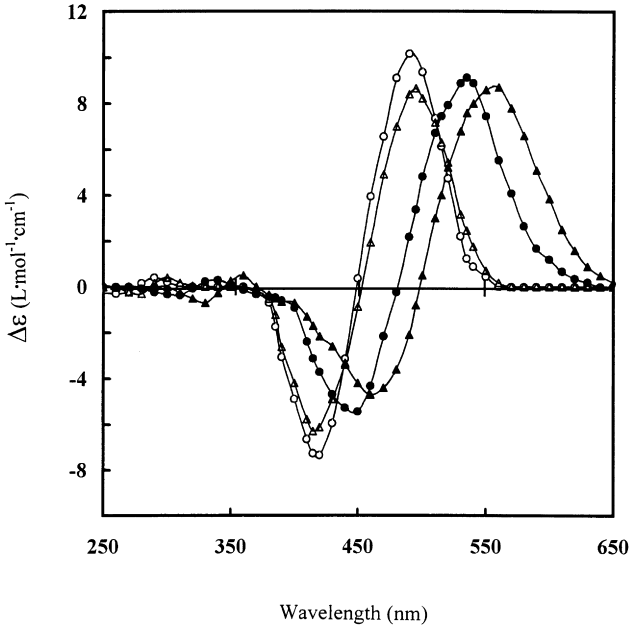


Fig. 3. CD spectra in DMA of poly[(*S*)-**MAP-C**] (-○-), poly[(*S*)-**MAP-F**] (-△-), poly[(*S*)-**MAP-S**] (-●-) and poly[(*S*)-**MAP-D**] (-▲-).

Table 4
Microtacticity of polymeric derivatives as determined by ^{13}C NMR (P_m and P_r represent the probability of formation of *meso* and *racemo* dyads; *mm*, *mr*(*rm*) and *rr* are the percent amounts of triads present in the polymers; $P_{m/r}$, $P_{r/m}$, $P_{m/m}$ and $P_{r/r}$ are the calculated probabilities that a given dyad follows a dyad having the same or the opposite relative configuration)

Polymer	P_m	P_r	*mm* (%)	*mr*(*rm*) (%)	*rr* (%)	$P_{m/r}$	$P_{r/m}$	$P_{m/m}$	$P_{r/r}$
Poly[(*S*)-**MAP-C**]	0.26	0.74	7	40	53	0.27	0.73	0.26	0.73
Poly[(*S*)-**MAP-F**]	0.26	0.74	7	39	54	0.26	0.74	0.26	0.74
Poly[(*S*)-**MAP-S**]	0.29	0.71	9	41	50	0.29	0.71	0.31	0.70
Poly[(*S*)-**MAP-D**]	0.26	0.74	7	39	54	0.26	0.74	0.26	0.74

group [4], appears to remarkably increase the dichroic effects, thus suggesting that the presence of moieties with high dipole moment values does not disfavor the establishment of chiral conformations of the macromolecules, in agreement with the above made considerations based on the UV spectra, indicative of a parallel arrangement of the chromophores.

The remarkably enhanced optical activity of the polymeric derivatives with respect to their monomeric counterparts could in principle be ascribed also to the occurrence of main chain stereoregularity originated by a prevalent microtacticity of the repeating units, although the radical polymerization process of methacrylates usually produces essentially heterotactic macromolecules with 60% of syndiotactic triads [39]. Indeed, the microtacticity of poly[(*S*)-**MAP-X**]s, as evaluated by integration of the distinct ^{13}C NMR signals originated by the methacrylic methyl group belonging to *meso-racemo* (*mr*) and *racemo-racemo* (*rr*) triads, respectively [14], accounts for the presence of 50–54% of *rr* (syndiotactic) triads (Table 4), indicative of a substantially stereoirregular structure with a predominance of syndiotacticity.

The results reported in Table 4 are in good agreement with those recently found for radically prepared poly(methyl methacrylate) macromonomers [40] and confirm that the radical polymerization of (*S*)-**MAP-X** monomers follows a Bernoullian statistics, as suggested by the close similarity of $P_{r/m}$ with $P_{r/r}$ (probability for a *r* dyad to follow a *m* or a *r* dyad) and of $P_{m/r}$ with $P_{m/m}$ (probability for a *m* dyad to follow a *r* or a *m* dyad) (see Experimental Part for details). It can be therefore concluded that the relevant optical activity of polymeric derivatives disclosed by CD spectra is essentially originated by the conformational dissymmetry of the macromolecules rather than by a predominant configuration of the stereogenic centers located in the methacrylic main chain.

4. Conclusions

The presence in optically active polymethacrylates of a rigid chiral moiety of one prevailing absolute configuration interposed between the main chain and the azoaromatic chromophore bearing a donor–acceptor conjugated system, favors the assumption by the macromolecules in solution of chiral conformations of one prevailing helical handedness, at least for chain sections, as indicated by the occurrence, in the CD spectra, of strong dichroic effects which are absent in the spectra of the corresponding low molecular weight model compounds, representative of the repeating unit of the polymer, devoid of conformational restraints. These effects originate from interactions involving the azoaromatic chromophores disposed according to a helical geometry of one prevaling chirality and induce the chromophores to assume an approximately parallel orientation. Indeed, the presence in polymeric derivatives of a blue shift of the UV absorption maximum with respect to the low molecular weight model compounds, confirms that the side-chain azoaromatic chromophores are arranged in solution, to some extent, as H-aggregates with a parallel orientation allowing the occurrence of mutual dipolar interactions, which can be considered of intramolecular nature in consequence of the low concentration of the substrate. This behavior appears to be due to the conformational stiffness of the macromolecules, particularly favored by the presence of the rigid pyrrolidine ring connecting the chromophore to the polymer backbone, as indicated by the remarkably high T_g values of these materials. Further research aimed at clarifying the structural features of the above described polymeric systems, particularly in the solid state, is currently in progress.

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References

[1] Angiolini L, Caretti D, Carlini C, Salatelli E. Macromol Chem Phys 1995;196:2737.
[2] Angiolini L, Caretti D, Giorgini L, Salatelli E. Enantiomer 1998;3:391.
[3] Angiolini L, Caretti D, Giorgini L, Salatelli E. Macromol Chem Phys 2000;201:533.
[4] Angiolini L, Caretti D, Giorgini L, Salatelli E. J Polym Sci, Part A Polym Chem 1999;37:3257.
[5] Kim N. Macromol Symp 1996;101:235.
[6] Prasad PN, Williams DJ. Introduction to nonlinear optical effects in molecules and polymers. New York: Wiley, 1991.
[7] Xie S, Natansohn A, Rochon P. Chem Mater 1995;5:403.

[8] Burland DM, Miller RD, Walsh CA. Chem Rev 1994;94:31.
[9] Verbiest T, Kauranen M, Persoons A. J Mater Chem 1999;9:2005.
[10] Perrin DD, Armarego WLF, Perrin DR. Purification of Laboratory Chemicals. Oxford: Pergamon, 1966.
[11] Compaigne E, Budde WM. Org Synth 1963;4:31.
[12] Shoondorp MA, Shouten AJ, Hulshof JBE, Shuddle EP, Feringa BL. Recueil Trav Chim Pays-Bas. 1994;113:250.
[13] Robello DR, Dao PT, Schildkraut JS, Scozzafava M, Urankar EJ, Willard CS. Chem Mater 1995;7:284.
[14] Peat IR, Reynolds WF. Tetrahedron Lett 1972:1359.
[15] DiMarzio EA, Dowell F. J Appl Phys 1979;50:6061.
[16] Natansohn A, Rochon P, Gosselin J, Xie S. Macromolecules 1992;25: 2268.
[17] Meng X, Natansohn A, Rochon P. Supramol Sci 1996;3:207.
[18] Altomare A, Ciardelli F, Ghiloni MS, Solaro R, Tirelli N. Macromol Chem Phys 1997;198:1739.
[19] Hallas G. J Soc Dyers Colour 1994;110:342.
[20] Chu KY, Griffiths J. Tetrahedron Lett 1976:405.
[21] Pushkara Rao V, Jen AK-Y, Wong KY, Drost KJ. J Chem Soc, Chem Commun 1993:1118.
[22] Chiellini E, Solaro R, Galli G, Ledwith A. Macromolecules 1980;13:1654.
[23] Majumdar RN, Carlini C. Makromol Chem 1980;181:201.
[24] Carlini C, Gurzoni F. Polymer 1983;24:101.
[25] Tinoco Jr. I. J Am Chem Soc 1960;82:4785.
[26] Okamoto K, Itaya A, Kusabayashi S. Chem Lett 1974:1167.
[27] Ciardelli F, Aglietto M, Carlini C, Chiellini E, Solaro R. Pure Appl Chem 1982;54:521.
[28] Meng X, Natansohn A, Barrett C, Rochon P. Macromolecules 1996;29:946.
[29] Brown D, Natansohn A, Rochon P. Macromolecules 1995;28:6116.
[30] Shimomura M, Ando R, Kunitake T. Ber Bunsenges Phys Chem 1983;87:1134.
[31] Shimomura M, Kunitake T. J Am Chem Soc 1987;109:5175.
[32] Schoondorp MA, Schouten AJ, Hulshof JBE, Feringa BL, Oostergetel GT. Langmuir 1992;8:1817.
[33] Schoondorp MA, Schouten AJ, Hulshof JBE, Feringa BL. Langmuir 1992;8:1825.
[34] Menzel H, Weichart B, Schmidt A, Paul S, Knoll W, Stumpe J, Fischer T. Langmuir 1994;10:1926.
[35] Dhanabalan A, Balogh DT, Riul JrA, Giacometti JA, Oliveira Jr. ON. Thin. Solid Films 1998;323:257.
[36] Dhanabalan A, Balogh DT, Mendonca CR, Riul JrA, Constantino CJL, Giacometti JA, Zilio SC, Oliveira Jr. ON. Langmuir 1998;14: 3614.
[37] Dhanabalan A, Dos Santos Jr. DS, Mendonca CR, Misoguti L, Balogh DT, Giacometti JA, Zilio SC, Oliveira Jr. ON. Langmuir 1999; 15:4560.
[38] Ciardelli F, Carlini C, Solaro R, Altomare A, Pieroni O, Houben JL, Fissi A. Pure Appl Chem 1984;56:329.
[39] Bovey FA. In: Allen G, Bevington JC, Booth C, Price C, editors. Comprehensive Polym Sci, Vol. 1. Oxford: Pergamon, 1989. p. 348.
[40] McCord EF, Anton WL, Wilczek L, Ittel SD, Nelson LTJ, Raffell KD. Macromol Symp 1994;86:47.