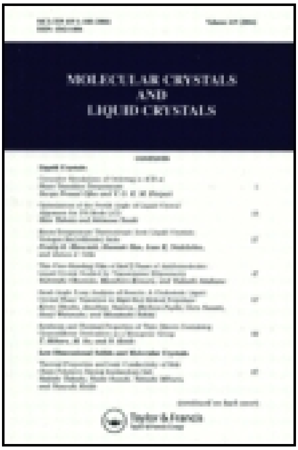

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Liquid Crystalline Properties of Linear and Network Polymers Containing Allyl Groups as Lateral Substituents

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Version of record first published: 24 Sep 2006

To cite this article: Ugo Caruso, Antonio Roviello, Augusto Sirigu & Carmela Troise (1999): Liquid Crystalline Properties of Linear and Network Polymers Containing Allyl Groups as Lateral Substituents, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 336:1, 1-15

To link to this article: http://dx.doi.org/10.1080/10587259908026017

Mol. Cryst. and Liq. Cryst., 1999, Vol. 336, pp. 1-15
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Printed in Malaysia

Liquid Crystalline Properties of Linear and Network Polymers Containing Allyl Groups as Lateral Substituents

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The synthesis and the mesomorphic properties of liquid crystalline polymer networks and the linear polymers upon which networks are based are reported. The linear polymers, synthesised from trimellitic acid, 2-allyl ester with the appropriate 4,4'-1,n diphenoxyalkane, exhibit a nematic mesophase, as indicated by calorimetric analysis, X-ray diffraction data, and polarising microscopy. Polymer networks were prepared from the linear polymers in the anisotropic state by thermal crosslinking in the bulk producing a very stable liquid crystalline phase.

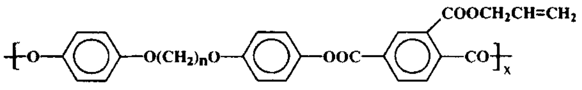
Keywords: mesogenic polymers; mesogenic networks

INTRODUCTION

A crosslinked liquid crystal is a peculiar monomolecular system whose structure may range from that of a rigid, irreversible anisotropic glass to that of a loosely crosslinked elastomer whose liquid crystalline order may reversibly be brought to isotropy by thermal treatment or solvent action. The intrinsic fundamental interest of such systems, and the possibility of developing practical applications on their basis has attracted increasing attention since several years[1-12]. Polymer networks with liquid crystalline order may be obtained in several different ways, either starting from low molecular weight mesogens or by crosslinking preformed, adequately functionalized linear mesogenic polymers.

Utilizing the latter approach, we have shown that networks exhibiting enantiotropic liquid crystalline behavior may be obtained even when crosslinking is operated in isotropic solution medium, provided that a sufficiently low crosslink density is maintained[8,11]. Quite recently, we have shown that crosslinking in the bulk of liquid crystalline fibrous samples, based on mesogenic linear polymers bearing unsaturated olephinic substituents at the mesogenic segments, may lead to macroscopically oriented mesomorphic networks[13].

In this article, the synthesis of linear polymers based on trimellitic acid esters corresponding to formula I, is reported. The liquid crystalline properties of these polymers and those of the networks derived from them by radical crosslinking are described.



$$\left[O-C_6H_4-O(CH_2)_nO-C_6H_4-OOC-C_6H_3(COOCH_2CH{=}CH_2)-CO \right]_x$$

Pn

$n = 2, 4, 8$

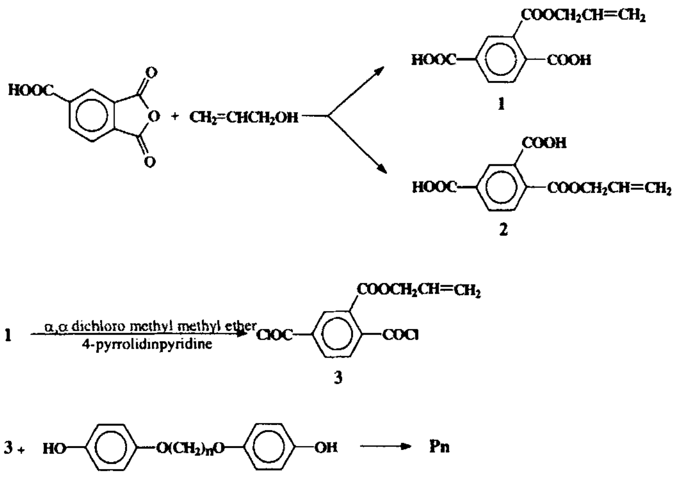
Formula I

EXPERIMENTAL

The polymer synthesis proceeds through the reaction of trimellitic acid 1,4-dichloride 2-allyl ester) with the appropriate 4,4'-1,n-diphenoxyalkane (scheme 1). Crosslinking takes place in the anisotropic state by use of a thermally activated peroxide initiator.

Synthesis of Precursors

Trimellitic acid, 2-allyl ester (**1**) was prepared from 1,2,4 benzenetricarboxylic anhydride and allyl alcohol, with the following procedure: 50g (0,260 mol) of 1,2,4 benzenetricarboxylic anhydride and 65 mL (0,955 mol) of allyl alcohol react for 3 hours at 120-130°C. At the end the reaction mixture is dissolved in 350 mL of boiling acetone and then 250 mL of toluene are added.



Scheme I

The solution is kept boiling to reduce its volume to ~300 mL. The white precipitate formed (the para isomer **1**) is retained on a Buchner funnel. The para isomer is further purified repeating this treatment utilising 300 mL of acetone and 200 mL of toluene. Subsequently, the compound is crystallised from a methyl alcohol/water (1:2) mixture. A final purification is performed by crystallising from a mixture of 200 mL water and 40 mL ethyl alcohol. (yield 9%). This compound melts at 230°C with sublimation. The ^{1}H-NMR spectrum, whose relevant data are collected in table I, is in accordance with the expected formula and the absence of meta isomer **2**.

Trimellitic acid dichloride 2-allyl ester **3** is obtained by reaction of 6.01g (0.0240 mol) of acid **1** with 32 mL (0.354 mol) of α,α dichloromethyl methyl ether and 0.36g (0.00243 mol) of 4-pyrrolidinpyridine at 80°C. The reaction proceeds until the solution becomes clear, then, after filtration, the remaining α,α dichloromethyl methyl ether is vacuum distilled. Dichloride **3** is distilled under reduced pressure (0.05 mmHg) at 220°C. ^{1}H-NMR data are collected in Table I. It is worth noting that a protracted heating under vacuum conditions produces a large amount of 1,2-benzene-tricarboxylic anhydride-4-acid chloride, as detected by ^{1}H-NMR spectroscopy (Table I). Compounds bis[[4,4'-(n-alkoxy)]phenol] with n= 2, 4, 8 were prepared by reaction of 1,n-dibromoalkanes with hydroquinone according to a procedure analogous to that described by Griffin and Havens[14]. Melting temperatures: n = 2, 226 °C (222-224°C[15]); n = 4, 205 °C; n = 8, 157°C. For all of them, ^{1}H-NMR spectra (Table I) are consistent with the expected formula.

Synthesis of polymers

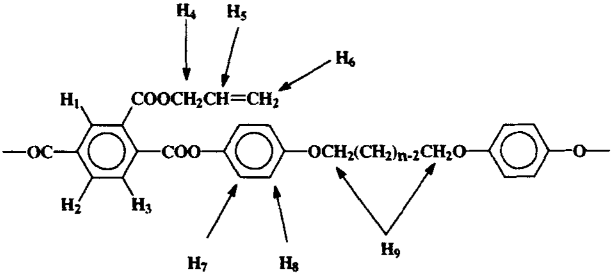
Polymers **Pn** (n = 2, 4, 8) have been synthesised in o-dichlorobenzene solution at reflux. **P4** has also been synthesised by the interfacial method, which was not applicable for **P2** and **P8**. The reason for this is related, for **P2,** to its low solubility in chlorinated solvents at room temperature and, for **P8**, to the low solubility of diphenol (n = 8) in the reaction conditions, combined with the quick hydrolysis of dichloride **3** in the alkaline aqueous solution required for the interfacial reaction, at a temperature allowing a sufficient solubility of diphenol n = 8. The synthesis of **P2** is reported as an example. 2.61976 g (0.0091 mol) of **3** and 2.24748 g (0.0091 mol) of biphenol (n = 2) react in 6.5 mL of o-dichlorobenzene (previously treated under molecular sieves) at reflux for two hours in nitrogen atmosphere. At the end, the polymer solution is added to 150 mL of cold n-hexane. The precipitated polymer is washed with n-hexane under stirring.

TABLE I. Some ^{1}HNMR data of intermediate and polymer compounds.

*	H_1	H_2	H_3	H_4	H_5	H_6	H_7	H_8	H_9
1	8.33d	8.27d*	7.94d	4.82d	6.03m	5.32d*			
2	8.51d	8.25d*	7.78d	4.80d	6.02m	5.31d*			
3	8.66d	8.37d*	7.76d	4.86d	6.02m	5.36d*			
tm	8.76d	8.65d*	8.22d						
b2							6.80m	6.69m	4.17s
b4,8							6.80m	6.69m	4.04t
P2	8.71	8.32	7.88	4.84	6.00	5.30	6.96	6.96	4.19
	8.86§		7.80§						
P4	8.70	8.40	7.90	4.85	6.01	5.28	7.15	7.00	3.98
P8	8.68	8.40	7.95	4.84	6.03	5.30	7.20	6.94	4.00
	8.80§		7.83§						

For atom labels refer to scheme II; δ (ppm); s = singlet; d =doublet; d*=pseudo-doublet, actually forming a AA'XX' multiplet; t = triplet; q = quadruplet; m = multiplet. *) compounds as from formula I and scheme I (tm = trimellitic anhydride; b2 , b4,8 = bis[[44'-(n-alkoxy)]phenol] (n = 2, 4, 8); §) meta isomer

To obtain **P4** by interfacial reaction, 5.08395g (0.0177 mol) of **3** is dissolved in 100 mL of cold chloroform and then added, under vigorous stirring, to a solution of 4,85764g (0.0177 mol) of biphenol (n = 4), 1.2g (0.0035 mol) of tetrabutylammonium hydrogensulfate in 200 mL of cold water; then, in one minute time, 2.57g (0.0704 mol, that is, twice the amount of **3** plus that of tetrabutylammonium hydrogensulfate) of potassium hydroxide, previously dissolved in 40 mL of cold water, are added to bring pH to ~8. After some minutes, as pH becomes slightly acid, it is restored to the starting value using an aqueous solution of sodium hydrogencarbonate. The reaction is stopped after about 5 minutes. In order to precipitate the polymer, 150 mL of cold n-hexane is added under stirring to the reaction mixture. The polymer was then repeatedly washed under stirring with water, chloroform/n-hexane 1/1 mixture, ethanol/water mixture and, finally, with boiling ethanol. All polymers have been dried under vacuum at 40 °C.



Scheme II

Polymer crosslinking

Crosslinking of **P2** and **P4** was performed heating a polymer mixture with t-butylhydroperoxide (3 wt%) in the DSC apparatus at 10 °C/min heating rate under nitrogen flow. The reaction occurs in the range 170-190°C, and is indicated by an exothermal signal. **P8** was crosslinked in a similar way using t-butylperoxide (3 wt%) as a radical initiator starting decomposition at ~ 110°C, so that the crosslinking reaction may take place, at least partially, as the polymer is in the anisotropic state. For this polymer, however, crosslinking was also performed under static conditions at 130 °C for 60 min.

For the characterisation of the phase behaviour, differential scanning calorimetry (DSC), polarising microscopy and X-ray diffraction techniques were employed.

For the DSC analysis, an indium calibrated Perkin Elmer DSC7 apparatus was utilised. Samples were examined under dry nitrogen atmosphere with a temperature scanning rate of 10 °C/min. The phase transition temperatures reported in the discussion section were measured at the maximum of the transition endotherms. A Mettler TG50 apparatus was utilized for thermal analysis of linear and crosslinked polymers.

Optical observations were performed on a Zeiss Axio-skop polarising microscope equipped with a Mettler FP5 micro furnace. X-ray diffraction patterns were recorded by the photographic method utilising a flat-film camera and the Ni-filtered CuKα radiation.

Intrinsic viscosity of a chloroform solution of polymer **P4** was measured utilising an Ubbelohde viscometer at 25.0 °C with the following result: **P4**(interfacial polymerization) $[\eta] = 1.2\ dLg^{-1}$, **P4**(solution polymerization) $[\eta] = 0.78\ dLg^{-1}$. Vapour pressure osmometry experiments utilising a Knauer apparatus were performed at 37.00 °C on chloroform solution for interfacially polymerized **P4** and at 120.0 °C on o-dichlorobenzene solution for **P2** and **P8**. For all polymers, the experiments indicate average molecular weights higher than the maximum instrumental limit (~20000).

RESULTS AND DISCUSSION

Linear polymers

Combined polarizing microscopy, DSC analysis and X-ray diffraction show that all linear polymers exhibit enantiotropic liquid crystalline behaviour of nematic structure. The chemical stability of the polymers in the absence of a crosslinking agent is high enough to allow heating them above isotropization temperature with no problems, and preserving solubility. Figure 1 shows the first DSC heating run of as prepared polymers.

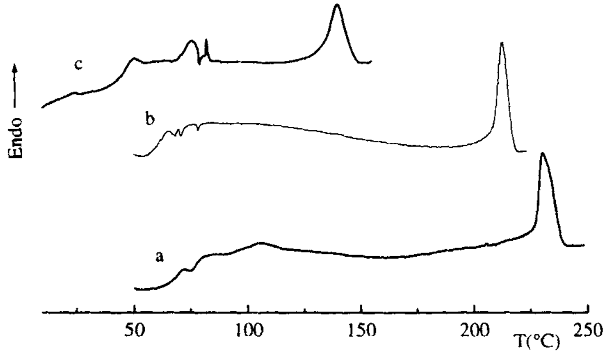


FIGURE 1 First DSC heating curve for P2(a), P4(b) and P8(c)

For a more sensible comparison, the curve for **P4** pertains to the solution prepared sample. (However, everything concerning **P4** will refer hereinafter to the interfacially synthesised polymer, unless is differently stated). Relevant thermodynamic data are reported in Table II. As prepared polymers are very poorly crystallized materials. Actually, melting transition is hardly detectable. For polymer **P2** (curve a) an endothermic DSC signal, probably due to melting, is detectable at ~100 °C with a virtually unmeasurable enthalpy change. However, annealing treatments, at 80, 100 and 110°C for 70 minutes, do not produce any detectable effect on crystallinity. The endothermic signals clearly shown in Figure 1 concern the nematic-isotropic liquid transition. Consistently, isotropization temperatures decrease with increasing length of the flexible spacer in the bakbone chain.

TABLE II Thermodynamic data for polymers Pn.

n	Tg (°C)	Tm (°C)	ΔHm (J/g)	Ti (°C)	ΔHi (J/g)
2	70	~100	n.d.	230	6.3
4	56	n.d.	n.d.	213	7.0
4 (a)	56	110	0.9	233	10.5
8	45	82	1.5	138	4.8

Tg = glass transition temperature; Tm = melting temperature; ΔHm = melting enthalpy; Ti= isotropization temperature; ΔHi= isotropization enthalpy;
(a) interfacial synthesis.

A similar feature appears with strictly analogous polymers containing the 2-alkanoxyterephthalic group in the mesogenic moiety[16] and is quite constantly observed in general for segmented chain semiflexible liquid crystalline polymers[17]. In Figure 2 the detailed DSC thermal behavior of interfacially synthesized **P4** is reported.

Curve a, concerning the first heating run, shows the glass transition signal at

56°C, the melting endotherm in the range 110-130°C, with ΔH = 0.9 J/g, and the isotropization peak at 233 °C with ΔH = 10.5 J/g. No crystallization takes place on cooling (curve b). Consistently, no melting signal is detectable in the second heating run (curve c). However, upon annealing at 110°C for 70 minutes, some crystallization takes place and the melting transition is clearly detectable at 126 °C (ΔH = 3.9 J/g) in the relative DSC scan (curve d).

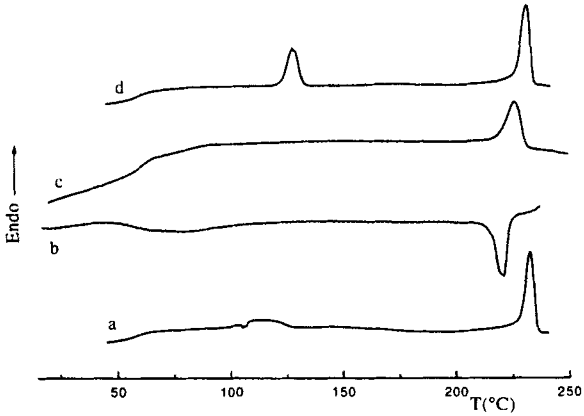


FIGURE 2 DSC thermal behavior of P4

It is apparent that some remarkable difference is to be observed, as compared to the solution prepared sample: isotropization temperature and isotropization enthalpy are significantly increased, and the phase transition temperature interval is narrowed. It is unlikely that this feature might be entirely traced to a difference in molecular weight and molecular weight distribution. In fact, the results of the vapour pressure osmometry experiments indicate that the average molecular weight of solution prepared polymers should be well off the range (Mn <~ 10,000) in which a dependence of the isotropization temperature on

Mn is usually observed[17]. A different and more convincing evidence is afforded by the ^{1}H-NMR spectra indicating the presence of about 5% of meta isomeric unit (Scheme I, formula **2**) in the structure of all solution synthesised polymers. No such feature is detectable for interfacially synthesized **P4**. The presence, even in small amounts, of meta isomer disrupts the linearity of the rigid polymer segment containing it, therefore reducing its mesogenic potential. This leads to a mesogen-nonmesogen copolymeric structure with a decrease of the isotropization temperature.

No detailed investigation has been performed to elucidate the chemical path of the observed isomerization. Seemingly, it involves the trimellitic acid dichloride 2-allyl ester **3** monomer, rather than the polymer (an interfacially synthesised sample of **P4**, brought in o-dichlorobenzene solution, and there kept at ~180 °C for two hours, does not undergo any detectable isomerization), and is quite evidently favoured by the reaction conditions.

The X-ray diffraction pattern, recorded at room temperature for polymer fibers obtained by extrusion in the liquid crystal phase, is characterized for all polymers by an equatorial halo centered at $\sin\theta/\lambda = 0.116 \pm 0.02$ Å^{-1}. A rather diffuse "four spot pattern" at $\sin\theta/\lambda = 0.034$ Å^{-1}, for **P4**, and at 0.024Å^{-1}, for **P8**, indicates some cybotactic structuration of the nematic phase at room temperature. This feature is smeared out at higher temperatures. The diffraction pattern of a fibrous sample of **P4** recorded at 160 °C shows only a diffuse equatorial halo with intensity maximum at $\sin\theta/\lambda = 0.111$ Å^{-1}. No evidence for a cybotactic structure is detectable for **P2**, even at room temperature. Annealing has a clearly detectable effect only for **P4**. The diffraction pattern recorded at room temperature for a fibrous sample previously annealed 70 min at 110 °C shows a sharp equatorial diffraction at $\sin\theta/\lambda = 0.114$ Å^{-1}, superimposed to the cybotactic nematic pattern. The evidence that some crystallization has occurred is also detectable by DSC means (Figure 2, curve d). In conclusion, the X-ray diffraction data are consistent with a nematic structure for the liquid crystal phase. The same conclusion is supported by a different evidence: shearing the liquid polymers in the mesophase produces a "band structure" morphology clearly detectable by polarizing microscopy.

Polymer networks

All polymers have been crosslinked in bulk in the presence of ~3% radical initiator. Networks have been kept swelling for at least 7 days in a large volume excess of o-dichlorobenzene at room temperature. At this stage, a small percentage of the original polymer (~3%) is found in the solvent as uncrosslinked material and is taken away. The swollen network of **P8** has a polymer content of 8% or 13% by weight according to wether it was crosslinked under dynamic or static (60 min at 130 °C) conditions. In both cases it is optically isotropic at room temperature and has a rubbery consistency. Remarkably different are the properties of the swollen networks of **P2** and **P4**. They are optically anisotropic, and the polymer content is as high as ~60% by weight. This largely exceeds the room temperature solubility of the linear polymers and indicates that the observed optical anisotropy is not to be related to the formation of a homogeneous liquid crystalline solution but to the presence of phase separation including an anisotropic "solid" polymer phase[18].

The X-ray diffraction pattern, recorded at room temperature for crosslinked **P2** in the swollen state indicates absence of crystallinity and is consistent with a nematic structure of the anisotropic phase. As to the unswollen networks, which are obtained by solvent extraction in vacuum at room temperature, **P2**, **P4**, and statically crosslinked **P8**, exhibit a persistent optical anisotropy up to incipient decomposition temperature (> 300 °C). For these polymers, however, an endothermic DSC signal is clearly detectable at temperatures around 230-250 °C, for **P2** and **P4**, and in the range 130-150 °C, for **P8**; that is, somewhat higher than the isotropization temperature of the corresponding linear polymers. This feature does not change (qualitatively and quantitatively) for networks that have not been subjected to solvent extraction.

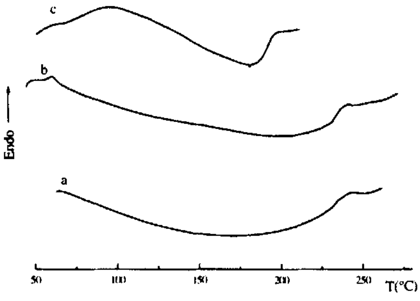


FIGURE 3 DSC behavior of crosslinked P4

The DSC behavior of crosslinked **P4** is reported in Figure 3.(unextracted sample: curve a; previously solvent extracted sample: curve b; crosslinking run: curve c). X-ray diffraction data rule out the possibility that the calorimetrically detected endothermic effect might be related to a LC-nematic transition; LC being some hypothetical new liquid crystal phase formed on crosslinking. In fact, the diffraction pattern of the crosslinked material is virtually identical to that of the corresponding linear polymer. In conclusion, the observed effect is probably due to the concurrence of at least two factors such as: i) higher average crosslink density (**P2** and **P4** have shorter flexible spacers in the backbone chain), ii) inhomogeneity in the crosslink density caused by an uneven dispersion of the activator and favoured by a reduced conformational mobility of the backbone chains. Factor i) may be mainly responsible for the diffuse optical anisotropy, which persists at the highest temperatures, while factor ii) would produce low crosslink density small areas still capable of undergoing "local" isotropization only detectable by DSC means. In all cases, the higher isotropization temperature, compared to the linear polymer, found for all networks, is what one should expect when crosslinking takes place in the liquid crystal phase. Consistent with this picture appears to be the phase behavior of polymer **P8**, previously crosslinked along the DSC scan up to 145 °C at 10 °C/min temperature scan rate. This procedure implies that crosslinking takes place within the isotropization temperature range of the linear polymer and, presumably, that a lower crosslink density is attained.

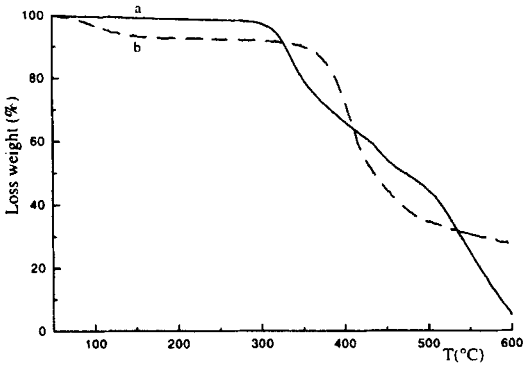


FIGURE 4 Thermogravimetric curves for P4. Linear polymer, curve a; network, curve b. Temperature scan rate 10 °C/min.

As a consequence, the isotropization of the crosslinked polymer is optically detectable in the range 135-145 °C and a DSC endothermic signal appears in the range 110-134 °C. The associated enthalpic change , 3.8 J/g, is significantly smaller than that measured for the linear polymer (4.8 J/g).

The thermal stability of the crosslinked polymers is significantly higher than that of the corresponding linear precursors. Figure 4 shows, as an example, the TGA diagrams for **P4** recorded in nitrogen atmosphere. For the linear polymer (curve a), the 5% weight loss temperature is ~320 °C. For the cross-linked polymer, previously subjected to swelling and extraction, as described above, a 6% weight loss, corresponding to complete solvent elimination, takes place within 120 °C, while, a further 5% loss is reached at 360 °C.

Acknowledgements

Research supported by Ministero dell'Università e della Ricerca Scientifica e Tecnologica and by Consiglio Nazionale delle Ricerche. NMR spectra were recorded at the "Centro Interdipartimentale di Metodologie Chimico Fisiche".

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