Synthesis and Physicochemical Characterization of Branched Poly (monomethyl itaconate)

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Abstract: The synthesis and characterization of branched polymers derived from poly (monomethyl itaconate) (PMMI) are reported. Important changes in the properties of the functionalized products were found with respect to the base polymer, establishing a close relationship with the hydrophobic/hydrophilic balance of the products. The intrinsic viscosity of the branched PMMI showed an increment in its hydrodynamic volume due to the insertion of branched molecules, which correspond to a first generation of dendrons. Their incorporation into the polymer chain caused a change in the surface energy values of the sample films and enabled the products to form stable monolayers at the air-water interface.

Keywords: branched polymers, branched molecules, monolayer, poly (monomethyl itaconate).

Introduction

Growing interest is quite noticeable in research directed toward molecules and macromolecules with multiple branched structures and a high concentration of functional terminal groups. It is also of great importance to realize that these groups can be modified in order to change the characteristics such as hydrophobicity, wetting, adhesion, and solubility. [1] It is known that the hydrophobic/hydrophilic balance in the branched product is controlled by the chemical composition either of arms or cores and branches. [2, 3]

The most commonly known class of highly branched molecules, dendrimers, has been intensively studied for two decades. Accordingly, numerous results related to chemical architectures, synthetic routines, encapsulating properties, nanocomposite materials and catalytic systems have been reported. [4, 5, 6] However, several factors limit the prospective use of conventional dendrimers for large-scale applications. The most important factor is the extremely high cost involved in the synthesis and purification causing unavailability of this material in large quantities. As a result, related highly branched structures, other than dendrimers, with potentially interesting properties have been introduced and studied in depth over the last years.

In addition to regular dendrimers, the most common branched architectures include graft, arborescent, hyperbranched and star-shaped types. Each of these comprises a wide variety of possible chain configurations and shapes which depend on the

synthetic path exploited, and on the chemical composition of backbones, cores, branches and terminal groups. One of the simplest, highly branched architectures introduced and studied for a long time is the graft polymer, also called molecular brush or comb (especially in the case of short side chains). [7] Those with dendritic branches connected to the backbone are called dendronized [8, 9] or jacked polymers. [10] Therefore, various polymer dendronization strategies have been developed on the basis of classical organic and inorganic chemistry. [11-17] One of such strategies consists in the production of polymers with dendron side groups using pre-synthesized dendritic building blocks, which are attached to a reactive polymer chain. The architecture of this macromolecule is then characterized by a rigid [18, 19] or a flexible [20] backbone wrapped around by wedges that increasingly branch as they go from the inner to the outer regions. Depending on backbone stiffness, degree of coverage, and fragment size, the envelope of these macromolecules varies.

In a previous work, [21] we presented the study of the hydrophobic/hydrophilic balance of a family of dendrons synthesized in our labs bearing a different number and nature of functional groups on their surface. The selection of the structure in the construction of these molecules was based on a synthetic strategy to generate a branched effect on the properties of the resulting building block and the subsequently constructed product. Similarly, we reported [22] the use of some of those grafting molecules to modify the chemical/physical properties of hydrophobic methyl phenyl diisocyanate (MDI) oligomers.

In this study, we present the synthesis and characterization of new branched polymers based on poly (monomethyl itaconate), a hydrophilic and water-soluble polymer of high molar mass through a fast and simple pathway. The branched molecules used as grafting agents correspond to the first generation of a family of dendrons synthesized by us and previously mentioned, which were selected because of the polarity of their surface functional groups. The physicochemical properties of the functionalized polymers will be studied and their surface and interfaces behaviour will be compared with that of the base polymer and related to the nature of terminal groups of the branched molecules.

Results and discussion
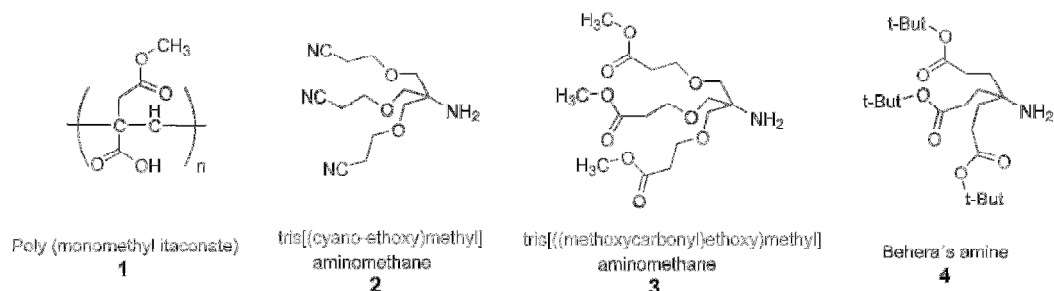
Synthesis of branched polymers

The functionalization was carried out by forming amide bonds between the activated carboxylic acid group from PMMI and the primary amine group from branched molecules. Dicyclohexylcarbodiimide (DCC) was used as an activating agent and 1-hydroxybenzotriazol (HBT) as catalyst. Three different branched molecules were used, tris[(cyano-ethoxy)methyl]aminomethane (**2**), tris[((methoxycarbonyl)ethoxy)methyl] aminomethane (**3**) and Behera's amine (**4**), to afford products **5**, **6** and **7**, respectively. Figure 1 shows the structures of the PMMI and branched molecules used and Scheme 1 displays the route to obtain branched polymers **5**, **6** and **7** from PMMI using molecules **2**, **3** and **4**, respectively.

The optimal molar ratio found was with MMI:DCC:HBT:branched molecules 10:1:1:4.

Table 1 summarizes the functionalization degree of the branched products obtained by elemental analysis and ^{1}H-NMR. In all cases the incorporation of the branched molecules as side pendant groups of polymer chains was partial and the percentages observed were between 5.6% and 25.0%. The best functionalization degree found

was for **5**, probably due to greater compatibility and affinity between the polarity of the branched molecules and the polymer backbone.
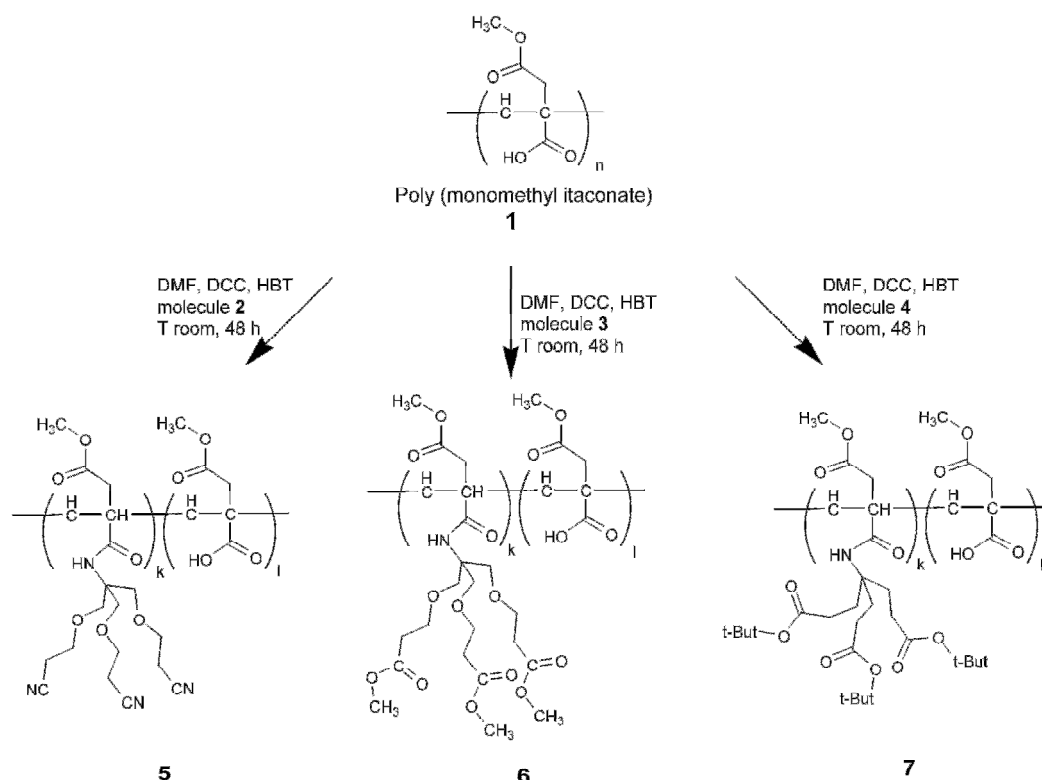
Figure 1. Structure of PMMI and branched molecules.

Poly (monomethyl itaconate) **1** tris[(cyano-ethoxy)methyl] aminomethane **2** tris[((methoxycarbonyl)ethoxy)methyl] aminomethane **3** Behera's amine **4**

Scheme 1. Synthesis of branched PMMI

Table 1. Dendronization degree calculated by elemental analysis and NMR

| Product | Mol of MMI monomer/ Mol of Dendron | | Average dendronization degree (%) |
	Elemental analysis	^{1}H-NMR	
5	6	4	25.0
6	13	13	7.7
7	18	18	5.6

Through the analysis of ^{1}H NMR spectra, the formation of new bonds was confirmed, by which we analysed the chemical shift of the proton signals attached to the carbon bound to the amine group of each branched molecule (RHNC***CH***$_2$), and the carbon signals bound to the amino group (RHN***C***CH$_2$).

According to Table 2, the behaviour observed for these branched products is

analogous to that found for the same signals in amidation reactions performed to other branched products synthesized by us, in which the same branched molecules were employed.[16, 22]

Table 2. Signal shift in ^{1}H-NMR spectra of in DMSO-d_6

RMN [1]H	Branched molecule	δ (ppm)	Product	δ (ppm)
RHNCC**H_2**	2	3.32	5	3.41
	3	3.27	6	3.35
	4	1.43	7	1.68
RMN [13]C				
RHN**C**CH$_2$	2	55.4	5	58.1
	3	56.0	6	51.8
	4	52.0	7	56.9

The branched products were soluble in different solvents and important changes in solubility with respect to PMMI were noticeable. The solubility of the products in different solvents is summarized in Table 3. These results demonstrated a clear tendency: branched molecule **2** with polar functional groups on their surface leads to branched polymers soluble in polar solvent, whereas branched molecules with apolar functional groups (**4**) gives products soluble in apolar solvent. Therefore, the solubility studies of the functionalized polymers showed that as the hydrophobicity of the functional groups in the branched molecules increases, the functionalized products begin to be soluble in solvents of lower polarity. The opposite was observed for branched molecule with functional groups of higher hydrophilicity.

Table 3. Solubility of the different products.

Solvent	Product 5	PMMI	Product 6	Product 7
Water	+	+	+	-
Dimethylsulfoxide	+	+	+	+
Methanol	-	+	+	+
Tetrahydrofuran	-	-	-	+
Methanol/chloroform 25/75	-	-	-	+
Toluene	-	-	-	+

+ soluble

- insoluble

Intrinsic viscosities

Table 4 shows the intrinsic viscosity values [η] of the branched polymers and PMMI in dimethylsulfoxide. An important increase in the hydrodynamic volume of all functionalized polymers, **5**, **6** and **7**, compared to PMMI can be found due to the incorporation of the branched units. There are two possible explanations for this. First, DMSO may have a different thermodynamic power for each product. [25] Second, this increase could be due to the conformational changes of the branched polymers as a result of steric hindrance (rigid and expanded structures) after functionalization reactions. However, among branched polymers, product **6**, which showed the highest degree of functionalization using branched molecule 2 (with polar

functional groups in the surface), presented the lowest hydrodynamic volume. This behaviour may be explained by the affinity between the branched molecule 2 and the chain, both with high hydrophilicity, which leads to greater penetration and entanglement. Consequently, product **6** present a low hydrodynamic volume and this product may have therefore a pseudo-globular shape.

Table 4: Intrinsic viscosity values for PMMI and products dendronized in dimethylsulfoxide at 25º C.

Product	[η] dL g^{-1}
PMMI	0.78
5	2.53
6	3.39
7	3.29

Surface Energy

The effects of molecular architecture and end-group functionality on the surface properties of branched polymers were investigated [26]. The surface behaviour of hyperbranched polymers was previously observed by Mackay et al. in polymers substituted with hydroxyl groups and different alkenes. [27] They were the first authors to show that the melt surface tension of hydroxyl terminated HPBs was high and resembled that of water. In contrast, the surface tension of HBPs terminated with alkyl end groups was similar to that of linear polyethylene. Table 5 summarizes the total surface energies (SE) of the products under study. In our products, an increase in the SE of the branched polymers with respect to that of PMMI was observed. This result may indicate that the expression of chain ends at surface level is likely to depend on the nature of end groups and the branching density of the polymer backbone. [29] These results suggest that terminal segments of branched polymers **5**, **6** and **7** give rise to rigid and expanded polymeric structures. Therefore, due to the low mobility of chain segments or to the affinity of branched molecules for the base polymer, those end groups accommodated themselves in the interior of the molecule preventing their migrating to the surface and increasing the SE. Similarly, product **5**, with high affinity between branched molecules and chains, showed the highest SE; in product **7** the opposite was observed. These findings are in agreement with the results found from solubility studies.

When the individual components of SE between branched polymers were analysed and compared with the PMMI, interesting differences were found. The dispersion force contribution γ^d and the polar contribution γ^p to the total surface energy were calculated using the Owens-Wendt-Kaeble methods. [28, 29] The dispersion force contribution γ^d was approximately constant for products **5, 6 and 7,** but the polar component γ^p showed a larger variation depending on the nature of end groups. It is clear that the end groups of grafting molecules have more important effects on γ^p than on γ^d. The products with tert-butyl end groups, mostly of hydrophobic nature, showed the lowest γ^p and are expected to migrate mostly to the air interface to minimize the SE. The other extreme, the branched polymers with nitrile-terminated groups, the most hydrophilic polymers, showed the highest γ^p, so the highest SE was observed. In the middle, methyl end group product had an intermediate SE.

Table 5: Total surface energy SE, dispersion contribution γ^d and polar contribution γ^p for the polymers studied.

| Polymer	SE (mN m^{-1})	γ^d (mN m^{-1})	γ^p (mN m^{-1})
5	55.1	23.5	31.6
6	53.1	23.1	30.0
7	51.9	22.8	29.1
PMMI	50.7	26.9	23.8

Monolayers at the air-water interface and surface pressure/area

Polymer monolayers spread at the air-water interface were studied using the Langmuir Technique. All functionalized polymers showed a capacity to organize and form monolayers at the air-water interface in contrast to the PMMI base polymer, which did not form a monolayer under the same conditions. These results indicate that branched products have the capacity to stabilize the monolayer formation. Figure 2 shows the Langmuir isotherms obtained by monolayer compression of the functionalized polymers at the air-water interface. The surface pressure π increases gradually by monolayer compression. The functionalized products **5**, **6** and **7** showed a similar behavior at the air-water interface. In Figure 2, three different qualitative regions in the isotherms can be observed: at low surface concentration, π increases slowly as the monolayers are compressed; in the semidilute region, as the pseudo liquid state is reached, π rises rapidly; and at high surface concentration the condensed stated is reached and $\square$ increases faster, before the collapse. In products **5** and **7,** the liquid phase is observed between 0.5 to 0.9 cm^2. mg^{-1} and the condensed state from 0.25 cm^2. mg^{-1} before the collapse. For product 6, the liquid phase is from 0.4 to 0.7 cm^2. mg^{-1} and the condensed state from 0.25 cm^2. mg^{-1} before the collapse. A phase transition could be observed in the three cases which results from a liquid expanded to a more condensed phase change.

In analyzing the collapse pressure of the different products, we can see that it is higher for product **7** (with hydrophobic functional groups), in agreement with the results found in surface energy studies. Therefore, a high surface pressure is required for the collapse of the monolayer when the superficial tension is lower. Figure 2 shows that the surface area of the three products at the collapse pressure is the same. To account for this, we may assume that at high surface pressure, the behavior of branched polymers is governed by the backbone of the base PMMI, which is the same for all branched products. According to these results, water could interact with the pending polar groups of branched molecules and with the free acid groups of the polymer backbone, by which characteristic expanded isotherms are obtained. This interaction is possible only if the branched molecule adopted a conformation exposing the polar groups to the water subphase, and the backbone of the PMMI and other apolar moieties (*tert*-butyl ester of pendant units or methyl groups of pendant units or of the backbone) to the air subphase

A more rigorous and comparative study on the behavior of different branched products would not be quite possible due to the differences found between their branched grade and molecular weight.

Figure 2. Langmuir isotherms of branched PMMI, a- Surface pressure vs specific area, b- Surface pressure vs surface concentration
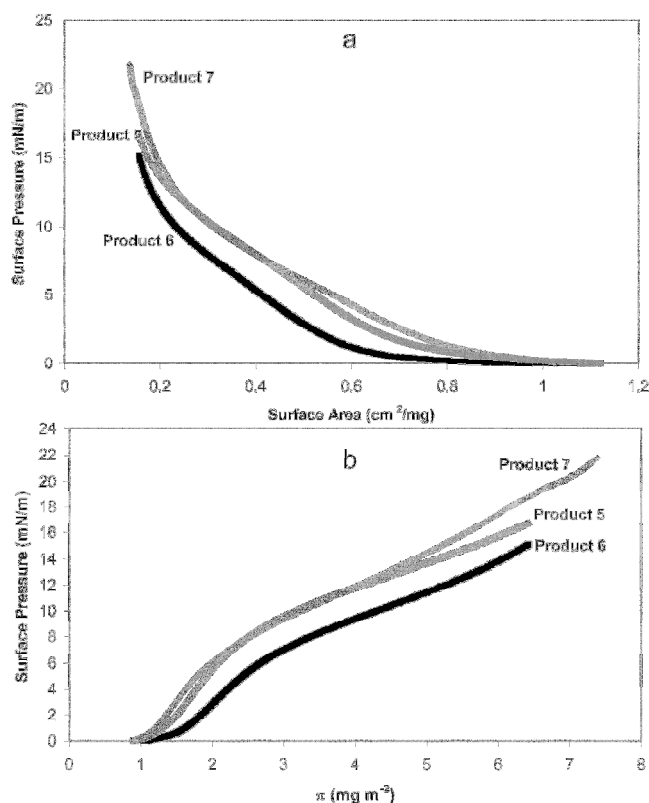
Experimental part

Materials

Substrate 5-nitroisophthalic acid was obtained from Sigma; tris-(hydroxymethyl)-aminomethane (TRIS) from Anedra; acrylonitrile from Carlo Erba; silica gel 60 from Merck. Triethylamine, TEA 99% from Anedra; thionyl chloride from Merck; Behera's amine was kindly supplied by Newkome labs. Dicyclohexylcarbodiimide (DCC), 1-hydroxybenzotriazole (HBT), potassium bromide 99% FT-IR grade (Aldrich) and DMSO-d_6 99.8%D from Aldrich. All commercial chemicals were used without purification. Solvents were obtained from Sintorgan, purified by distillation, and dried with 4Å molecular sieves when necessary.

Methods

Polymer synthesis

An unfractionated poly (monomethyl itaconate) (PMMI) was obtained by polymerization of monomethyl itaconate (MMI) at 70º C in bulk under N_2 in the presence of 2,2'-azobisisobutyronitrile (AIBN), following a previously reported procedure. [23]

The PMMI was obtained from the fractioned precipitation of the PMMI unfractionated and synthesized as described above. The second fraction, which we call PMMI (**1**), was used for the chemical modification; it represented 79% of the initial mass. The molar mass of this sample was determined by its viscosity using parameter values previously measured. [23] The viscosity- average molar mass was 7.25 10^5 Da.

7

Branched molecules tris[(cyano-ethoxy)methyl]aminomethane (**2**) and tris[((methoxycarbonyl)ethoxy)methyl]aminomethane (**3**) were synthesized and characterized following a previously reported procedure [30]. Behera's amine **4** was kindly supplied by Newkome labs.

Functionalization

Branched polymers **5**, **6** and **7** were obtained through a typical carbodiimide-mediated process. The procedure consisted in the careful dropwise addition of a solution of DCC and HBT to a PMMI, after which the corresponding branched molecule was dissolved in *N,N'*-dimethylformamide (DMF). The ratio used was MMI:DCC:HBT:branched molecules 10:1:1:4. Then, the mixture was stirred for 48 h at room temperature. In all cases, the dicyclohexylurea, formed as a side product, was verified as a precipitate, which was filtered. Diethylether was added to the remainder, and the formation of a precipitate was verified again, which was separated and dried in vacuo. The solid obtained was washed with diethyl ether and dried under high vacuum.

Branched Polymer Characterization

Products were characterized by Fourier Transform Infrared Spectroscopy (FT-IR) on KBr discs using a Nicolet 5-SXC FT-IR spectrometer, and by ^{1}H-NMR and ^{13}C-NMR in DMSO-d_6 using a NMR Bruker Avance 400MHz Ultrashield spectrometer.

The main characteristic bands in the FT-IR spectra of PMMI were: 3503.5 cm^{-1} (s, OH stretching), 3009.6 and 2959.7 cm^{-1} (w, C-H stretching), 1734.1 cm^{-1} (s, C=O stretching), 1268.1 cm^{-1} (s, C-O stretching) and 923 cm^{-1} (m, OH bending vibrations). Changes in the FT-IR spectra were not observed for the branched polymer due to the high intensity of absorption bands of PMMI. The main changes in the branched products were observed for a widening of the band corresponding to C=O, between 1600 and 1800 cm^{-1}.

^{1}H-NMR and ^{13}C-NMR spectra of products **5**, **6** and **7** show the same pattern. The main signals corresponding to the PMMI and the signals characteristic of the branched units are summarized as follows:

signals corresponding to the PMMI structure:

^{13}C-NMR (DMSO-d_6) (δ ppm) = 171.9 overlapped (*C*=O ester and acid); 51.5 (O*C*H$_3$); 46.6 (CH$_2$*C*(COOH)(CH$_2$)CH$_2$ from polymer backbone); 43.2 (*C*H$_2$C(COOH)(CH$_2$)*C*H$_2$ from polymer backbone); 41.0 (C*C*H$_2$CO).

^{1}H-NMR (DMSO-d_6) (δ ppm) = 12.54 (broad, COO*H*); 3.44 (m, 2H, CC*H$_2$*CO) overlapped with 3.35 (s, 3H, C*H$_3$*); 2.50 (broad, 2H, C*H$_2$*C(COOH)(CH$_2$)C*H$_2$*).

Signals corresponding to branched units attached to PMMI:

Product **5**

^{13}C-NMR (DMSO-d_6) (δ ppm) = 119.6 (*C*N); 70.2 (C*C*H$_2$O); 66.4 (O*C*H$_2$CH$_2$); 58.1 (NH*C*CH$_2$O); 18.4 (CH$_2$*C*H$_2$CN).

^{1}H-NMR (DMSO-d_6) (δ ppm) = 3.63 (t, OC*H$_2$*CH$_2$CN); 3.41 (s, CC*H$_2$*O); 2.77 (t, OCH$_2$C*H$_2$*CN).

Product **6**

^{13}C-NMR (DMSO-d_6) (δ ppm) = 172.0 (*C*=O ester); 69.7 (C*C*H$_2$O); 67.2 (O*C*H$_2$CH$_2$); 51.8 (*C*NHCO); 51.6 (*C*H$_3$); 34.5 (*C*H$_2$COOCH$_3$).

^{1}H-NMR (DMSO-d_6) (δ ppm) = 3.64 (t, OCH_2CH$_2$); 3.61 (s, OCH_3); 3.35 (s, NCH_2OCH$_2$); 2.57 (t, CH_2CO).

Product **7**

^{13}C-NMR (DMSO-d_6) (δ ppm) = 171.3 (C=O ester); 80.5 (CH$_3$$C$O); 56.9 ($C$NHCH$_2$); 30.9 ($CH_2CH_2$CO); 29.0 (CH$_2$$CH_2$CO); 28.2 (OC$CH_3$).

^{1}H-NMR (DMSO-d_6) (δ ppm) = 2.26 (broad, CCH_2CH$_2$CO); 1.68 (broad, CCH_2CH$_2$CO); 1.40 (s, OC(CH_3)$_3$).

The functionalization degree of products **5**, **6** and **7** was obtained from elemental analysis carried out on a Fisons EA 1108 CHNS-O instrument and by ^{1}H-NMR data.

According to ^{1}H-NMR, the degree of grafted was obtained by comparison with the integral area of methylene (CH$_2$) and methyl (CH$_3$) groups from the polymer backbone at 3.44 and 3.35 ppm with respect to the area corresponding to the methylene groups (CH$_2$) of each branched molecule (2.77 ppm for **5**, 2.57 for **6** and 1.68 ppm for **7**).

Physical characterization

Solubility: the experiments were carried out dissolving each product in the selected solvent. In those experiments where non-soluble products were observed, these products were separated and weighted. Comparative results were tabulated in table 3.

Viscosities: they were determined using a capillary type Desreux-Bischoff [31] viscometer. Corrections for kinetic energy and shear rate were found to be negligible. Intrinsic viscosity [η] was calculated according to the classical empirical relations [32] in DMSO at 25º C.

Surface energies for cast films of the branched polymer samples on glass slides were determined by water and methylene iodide wettability measurements. A two-liquid geometric method was employed to determine the surface energy. [33] The static contact angles were measured at room temperature by a sessile drop technique, using a Dataphysics Optical Contact Angle measuring device, OCA 20. The contact angles were measured carefully from the left and right sides of the drop and subsequently averaged.

Surface pressure area^{-1} (π A^{-1}) isotherms of polymer monolayers on an aqueous subphase were studied using a Nima Model 611 surface film balance (NIMA Instruments, Coventry, UK). The entire system was covered with a box of poly (methyl methacrylate) in order to buffer temperature fluctuations and to prevent environmental perturbation. Monolayers were obtained by spreading a branched polymer fraction on the aqueous subphase from the chloroform/DMSO 50:50 binary solvent. In all cases the concentration of the spread solutions was 0.50 mg mL^{-1} and the temperature was 25º C. Water subphase was purified by Millipore Milli-Q system (resistivity greater than 18.0 MΩcm). A constant compression rate of 10 cm^2 min^{-1} was used in all experiments, these experiments were performed in triplicate to ensure their reproducibility.

Tg´s determination could not be make because it is known that poly(monoitaconate)s with pendant short chains doesn´t show Tg, or at least it is very difficult to get the Tg value by different techniques.[31, 32]

Conclusions

The functionalization of PMMI with three types of branched molecules of different polar characteristics was carried out and products with interesting modifications in their properties with respect to the base polymer were obtained.

The incorporation of the branched units with different surface functional groups results in a marked increase in the polymeric hydrodynamic volume and also in changes in the solubility. The surface properties of branched PMMI are likely to depend largely on the hydrophobic/hydrophilic nature of end groups. By varying the functionality of end groups, the surface properties of branched PMMI can be tuned over a range of surface energies. As expected, the increase in the hydrophilicity of end groups increased the surface energy. Lower surface energy products were obtained with hydrophobic terminated groups.

The branched products studied present an appropriate hydrophobic/hydrophilic balance and an adequate structural arrangement to obtain stable monolayers at the air-water interface. Therefore, it was possible to determine the effect of the functionalization using branched molecules, belonging to the first generation of a dendron family, which was directly related to the nature of functional groups present in their periphery (nitrile, methyl ester or *tert*-butyl ester).

These results demonstrated that functionalization and branching are useful tools for changing/modifying the properties of base linear polymers through a careful selection of the chemical structure and polarity of the branched units.

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