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Graft copolymers of propylene with styrene and methylmethacrylate: Structure, crystallization and thermal behaviour

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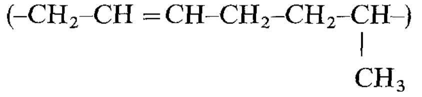
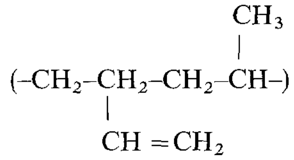
Nuclear magnetic resonance spectroscopy (NMR), differential scanning calorimetry (DSC), wide and small angle X-ray scattering (WAXS and SAXS) investigation have been used in order to achieve a molecular, thermal and structural characterization of a sample of propylene–butadiene copolymer containing 3% (wt/wt) of butadiene (uPP) and of uPP samples modified by grafting polymethylmethacrylate (upp–g–PMMA) and polystyrene (uPP–g–PS). The uPP copolymer was synthesized by Himont according to method patented by Himont [1], that allows, by means of the use of a proper catalyst system, co-polymers of propylene with diene having conjugated double bonds in which at least 20% of the unsaturations is of the vinyl type to be obtained. The influence of concentration, distribution and type of the uncrystallizable comonomer units on the thermal behaviour of such co-polymers and on the kinetic, morphologic and thermodynamic parameters related to crystallization process from melt have been also investigated.

1. Introduction

From the scientific and patent literature it is known that it is possible to copolymerize propylene with 1,3 butadiene in presence of a catalyst system [2–4] to obtain alternated or random copolymers with the following molecular structures in *cis* or *trans* type configuration



$$(-CH_2-CH=CH-CH_2-CH_2-\underset{\underset{CH_3}{|}}{CH}-) \qquad (1)$$



$$(-CH_2-\underset{\underset{CH=CH_2}{|}}{CH_2}-CH_2-\overset{\overset{CH_3}{|}}{CH}-) \qquad (2)$$

It is known, moreover, that the copolymers obtained by using Ziegler–Natta catalysts are characterized by a predominant 1, 4 addition of the 1, 3 butadiene units [2–4] and have, consequently, the double bond inserted in the main chain (see molecular structure 1). Such materials result, therefore, easily subject to thermal degradation and even more to oxidative degradation. From the patent of Cecchin and De Nicola [1], it emerges that the use of a proper catalyst system allows the configuration of the butadiene units to be controlled and copolymers of propylene with butadiene having the butadiene linked in configuration 1, 2 to be obtained (see molecular structure 2). Such materials show comparatively a higher stability; the vinyl type unsaturation, in fact, gives rise to no scission. Moreover, such copolymers can be cross-linked or modified by reactions typical of the unsaturated polymers or the allylic hydrogens, such as, for example, epoxidation, sulphonation, condensation with maleic anhydride, radicalic grafting of vinyl monomers, acrylic monomers, silanes, covulcanization with other unsaturated polymers, etc.

In the present paper we report on the results of nuclear magnetic resonance (NMR) spectroscopy, differential scanning calorimetry (DSC), wide and small angle X-ray scattering (WAXS and SAXS) investigations regarding a sample of propylene–butadiene copolymer containing 3% (wt/wt) of butadiene (uPP) and modified samples of such uPP obtained by grafting along its backbone chain polymethylmethacrylate (uPP–g–PMMA) and polystyrene (uPP–g–PS). Both uPP and uPP grafted copolymers have been synthesized in the Himont laboratories according to methods patented by Himont [1, 5]. The main goal of this study has been to achieve a molecular, structural,

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morphological and thermal characterization of the graft copolymers. Such a characterization will be essential in order to attain the final aim of the research, to assess the effectiveness of the graft copolymers investigated as compatibilizer agents in isotactic polypropylene (iPP)-based blends. In particular the effects of the addition of the uPP–g–PS copolymer in binary blends, constituted by (80/20 wt/wt) commercial samples of iPP and atactic polystyrene, and of the addition of the uPP–g–PMMA copolymer in binary blends, constituted by (80/20 wt/wt) commercial samples of iPP and polymethylmethacrylate, will be analysed in detail. This work will be undertaken in the framework of our research on iPP-based blends [6–9].

In the present paper, moreover, the influence of concentration, distribution and type of the uncrystallizable comonomer units on the thermal behaviour, on the morphology and structure of uPP, uPP–g–PS and uPP–g–PMMA copolymers and on the kinetic, morphologic and thermodynamic parameters related to the crystallization process from melt has been examined.

2. Experimental procedure

2.1. Materials

The starting polymers used in this study were an unsaturated copolymer of propylene containing 2.0% (wt/wt) of 1, 2 butadiene and 1.0% (wt/wt) of 1,4 butadiene (uPP) and graft copolymers of uPP with polymethylmethacrylate (uPP–g–PMMA) and with polystyrene (uPP–g–PS) synthesized in the Himont scientific laboratories using synthesis methods patented by Himont. The molecular characteristics of these materials are reported in Table I together with the degradation temperature in air (T_d(air)) and under nitrogen atmosphere ($T_d(N_2)$) obtained by thermogravimetric analysis according to the procedure reported below.

2.2. Techniques

2.2.1. Polymerization

The processes for obtaining random propylene–butadiene copolymers, in which at least 20% of the insaturations are of vinyl type, and for obtaining graft copolymers via metallation of the same, have been patented by Cecchin and co-workers [1, 5]. The synthesis of uPP was performed by copolymerizing a mixture of liquid propylene with a suitable amount of 1,3 butadiene, in presence of a stereospecific co-ordination catalyst, in a stainless steel autoclave equipped with a magnetic stirrer operating at 400 r.p.m. The catalyst system comprised a solid component consisting of titanium tetrachloride supported on activated magnesium chloride, and a 3/1 mol/mol triethylaluminium/diphenyl dimethoxysilane mixture. After injection of the catalyst complex into the autoclave the temperature was raised to 70 °C and kept constant throughout the reaction (4 h). The reaction was then stopped by addition of a few ml of an acetonic solution containing Irganox 1010, the unreacted monomers were removed by degassing and the unsaturated copolymer obtained was dried in an over at 60 °C in nitrogen stream.

The uPP so obtained was grafted with polystyrene or methylmethacrylate by metallation reaction and subsequent modification with the appropriated anionically polymerizable monomer. Metallation was performed by suspending 40 g of uPP in 400 ml of cyclohexane and treating the resulting slurry with 26 mmol of 1/1 mol/mol *n*-butyllithium (LiBu)/ *N*, *N*, *N'*, *N'*-tetramethylethylenediamine (TMDA) complex for 2 h at 60 °C under stirring. After washing (three times with 400 ml of cyclohexane), the metallated copolymer was resuspended in 400 ml of cyclohexane containing 20 ml of tetrahydrofuran (THF) and treated with 44 ml of styrene at 60 °C for 4 h under stirring.

The reaction was then stopped by adding a few drops of methanol, the grafted polymer washed repeatedly with hot cyclohexane and finally with hot methylethylketone until constant weight was reached.

Grafting with methylmethacrylate was conducted the same way as that for polystyrene, except that, in order to attenuate the reactivity of the carbanious and minimize side reactions with the polar monomer, 60 mol of diphenylethylene (in 150 ml of toluene) were added at − 78 °C to the metallated polymer suspended in 350 ml of THF prior to the addition of methylmethacrylate (40 ml); the grafting reaction was performed at − 78 °C for 4 h and then was left to continue overnight at room temperature.

Both metallation and grafting were carried out under dry nitrogen flow; glassware and solvents were treated according to the well-known techniques employed in anionic polymerizations.

2.2.2. NMR analysis

All NMR Spectra have been run in $C_2D_2Cl_4$ solutions (5% weight on volume) at 100 °C; in order to minimize crosslinking and instability effects fresh solutions were prepared for each spectrum. ^1H and ^{13}C NMR spectra have been run at 600.13 and 150.91 MHz on a Bruker AMX600 spectrometer or at 200.13 and 50.33 MHz on an AC200 spectrometer. Broad band decoupling was

TABLE I Molecular characteristics of uPP, uPP–g–PMMA and uPP–g–PS copolymers. Glass transition temperature of propylenic sequence (T_g) and degradation temperature in air (T_d (air)) and under nitrogen atmospher ($T_d(N_2)$ are also indicated

Sample	$[\eta]_{THM}^{135°C}$	% PMMA (wt/wt)	% PS (wt/wt)	T_g (°C)	T_d (air) (°C)	T_d (N_2) (°C)
uPP	1.59	–	–	12	209	333
uPP–g–PMMA	1.29	20	–	12	207	291
uPP–g–PS	1.37	–	35	7	225	312

performed with a Waltz sequence [10] for all directly detected carbon spectra, i.e. simple 1D and DEPT [11] spectra. ^1H–^{13}C heterocorrelated 2D spectrum was obtained by reverse detection [12].

2.2.3. *Thermogravimetric analysis*

Thermogravimetric analysis was carried out using a Mettler theromogravimetric analyser (TGA), model TG50. It consisted of a measuring cell, Mettler microbalance, and an Epson AX2 computer. The measurements were performed at a heating rate of 10 °C min^{-1} from RT to 500 °C in air and in nitrogen atmosphere in order to determine the temperature associated with possible thermally induced chain scissions of the materials.

2.2.4. *Differential scanning calorimetry*

The thermal behaviour of investigated materials was analysed by means of a Mettler TA 3000 differential scanning calorimeter (DSC) equipped with a control and programming unit (microprocessor TC10). The apparent melting temperatures (T'_m) and the crystallinity index of uPP, uPP–g–PMMA and uPP–g–PS copolymers, as obtained from synthesis, were determined by the following procedure . The samples were heated from RT up to 190 °C at a rate of 20 °C min^{-1} and the heat evolved during the scanning process (dH/dt) was recorded as function of temperature. The observed melting temperatures (T'_m) and the apparent enthalpies of melting (ΔH^*) were obtained from the maxima and the area of the melting peaks respectively. The crystallinity index was calculated from the ratios between the apparent enthalpies of melting and the enthalpy of melting of 100% crystalline iPP ($\Delta H^0 = 209\ J\,g^{-1}$).

The effect of nucleating ability of PMMA and PS chains grafted on the unsaturation of uPP copolymer on crystallization process of uPP copolymer was investigated following this procedure: the samples were heated from RT up to 190 °C and kept at this temperature for 10 min and then, they were cooled at a rate of 10 °C min^{-1}.

The apparent melting temperature (T'_m) and crystallinity indices of uPP, uPP–g–PMMA and uPP–g–PS copolymers isothermally crystallized at 112, 114, 116, 118 and 120 °C were determined following this procedure: the samples, heated to 190 °C at a rate of 20 °C min^{-1} and kept at this temperature for 10 min in order to destroy any trace of crystallinity, were rapidly cooled to the desired crystallization temperature (T_c); after complete crystallization such samples were again heated at 190 °C at a rate of 10 °C min^{-1}. The observed melting temperatures (T'_m) and the crystallinity indices of PP phase in uPP, uPP–g–PMMA and uPP–g–PS copolymers were determined as described above.

2.2.5. *Dynamic mechanical analysis*

In order to detect the glass transition temperature (T_g) of propylenic sequences of uPP, uPP–g–PMMA and uPP–g–PS copolymers dynamic mechanical tests were performed by means of a Polymer Laboratories Instrument analyser operating in flection at the frequency of 1 Hz on samples of copolymers melted at 200 °C and cooled at a rate of 2 °C min^{-1}.

2.2.6. *Optical microscopy*

The morphology developed in samples of uPP, uPP–g–PMMA and uPP–g–PS isothermally crystallized from melt was analysed by means of optical microscopy. A Leitz optical polarizing microscope fitted with a Mettler hot stage was used. The following procedure was employed: thin films, obtained by squeezing the materials between a microscope slide and a cover glass, were heated up to 190 °C and kept at this temperature for 10 min in order to destroy any trace of crystallinity; the temperature was then rapidly lowered to the desired T_c and the material allowed to crystallize isothermally. The radial growth rates of the observed spherulites were calculated by measuring the spherulite size as a function of time.

2.2.7. *Wide and small angle x-ray scattering studies*

Wide and small angle X-ray scattering (WAXS and SAXS) studies were performed on samples of uPP, uPP–g–PMMA and uPP–g–PS copolymers isothermally crystallized at 112, 114, 116, 118 and 120 °C. The WAXS studies were carried out by means of a PW 1060/71 Philips diffractometer (CuK_α Ni-filtered radiation) equipped with a sample spinner; the high voltage was 40 kV and the tube current was 30 mA. The SAXS studies were carried out by means of a compact Kratky camera equipped with a Braun sensitive positional detector. Ni-filtered CuK_α radiation generated from a Philips X-ray generator (PW 1730/10), operating at 40 kV and 30 mA, was used. The raw scattering data were corrected for parasitic scattering, absorption and slit smearing by using Vonk's method [13]. The desmeared intensities were then Lorentz factor corrected by multiplying by s^2 ($s = 2 \sin\theta/\lambda$ where θ is the angle between s, the atomic plane, and both the incident and reflected beams and λ is the wavelength of the X-rays) [14].

3. Results and discussion

3.1 ^1H AND ^{13}C NMR study of copolymers as obtained from synthesis process

^1H and ^{13}C NMR spectra of the butadiene–propene copolymer (uPP) show that the copolymer is essentially polypropene containing only a small amount of butadiene (~ 2% molar concentration). This butadiene is almost completely present as 1, 2 units; 1, 4 butadiene is present only as a trace. In fact in the spectroscopic double-bond region [15] only two sharp resonances are present at 145.1 p.p.m. and at 113.34 p.p.m., respectively due to the CH and to the CH_2 (see Fig. 1).

These resonances seem to be fully insensitive to chemical sequences. The total content of butadiene can be measured from the ^1H spectrum (not shown), since the absorptions in the spectoscopic region at

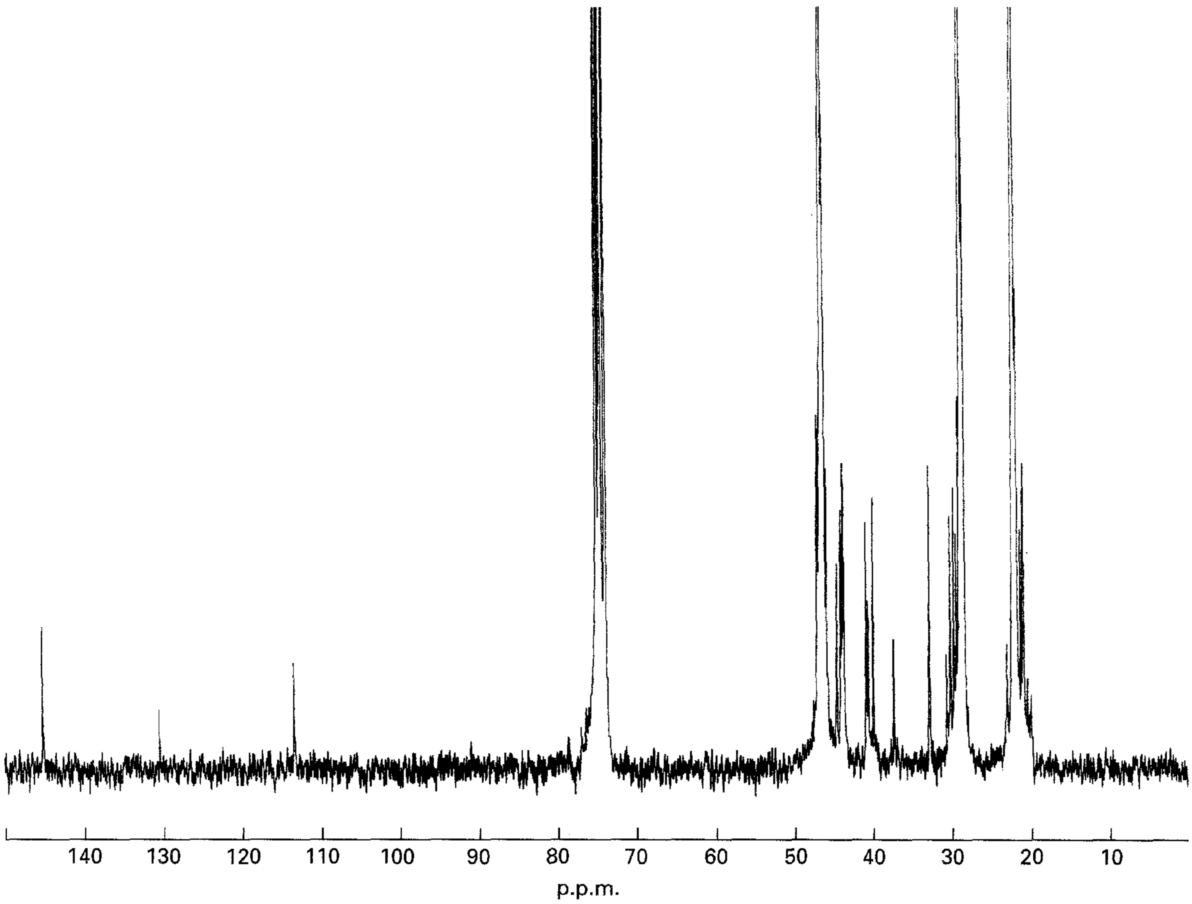


Figure 1 150.91 MHz ^{13}C spectrum of the copolymer propene–butadiene.

$\sim$ 5.5 p.p.m. are almost completely due to the three vinyl protons of 1,2 butadiene.

In the ^{13}C spectrum, in the aliphatic region of polypropene (20–50 ppm), many peaks can be observed; apart from the major unmodified polypropene resonances at 46.30, 28.70 and 21.85, these new peaks are due to the backbone of the butadiene–propene copolymer.

It must be noted that the backbone CH of a butadiene, compared to that of a propene unit, experiences an extra B downfield effect [16], causing a downfield shift ($\sim$ 39 p.p.m. in 1,2 polybutadiene, compared to $\sim$28.7 p.p.m. in polypropene); thus the methinic C of comonomers cannot give rise to any spectroscopic uncertainty.

Following this observation, in order to clarify the assignment of the copolymer peaks, DEPT experiments [11] were performed, (see Fig. 2). Here signals due to methylenic C atoms appear reversed on respect to methinic and methyls.

This experiment clearly shows the presence of four different CH of 1,2 polybutadiene, at 45.5, 43.4, 40.3 and 39.6 p.p.m. having comparable relative intensity. The peaks at 40.3 and 39.6 p.p.m. can be safely attributed to 1,2 polybutadiene in short blocks, possibly sterically disordered; in fact their chemical shift compares well with values reported in the literature [15] for the homopolymer.

Thus, the new extra CH peaks at 45.5 p.p.m. and at 43.4 p.p.m. must be due to 1,2 butadiene adjacent to propene units. This situation can occur within a regular head-to-tail triad propene–butadiene–propene or with an inversion in the insertion of one monomer; in fact this is due to the number and extent of gamma–gauche contribution by a $\sim$ 2–3 p.p.m. downfield shift [16, 17].

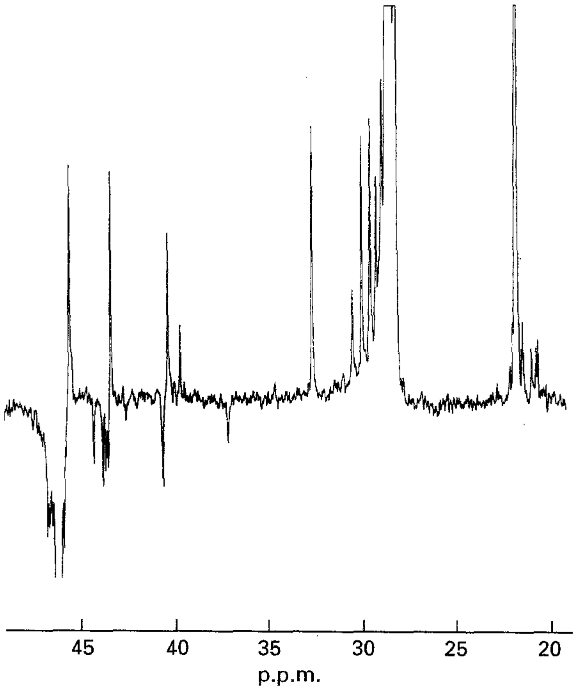
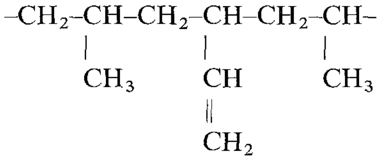


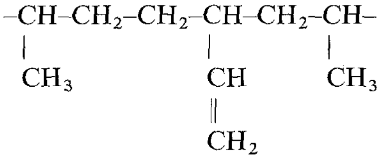
Figure 2 50.33 MHz ^{13}C DEPT.

Accordingly, the peak at 43.4 p.p.m. might be attributed to the following triad



$$\begin{array}{cccccc} -CH_2- & CH & -CH_2- & CH & -CH_2- & CH- \\ & | & & | & & | \\ & CH_3 & & CH & & CH_3 \\ & & & \| & & \\ & & & CH_2 & & \end{array}$$

While a possible attribution of the peak at 45.5 p.p.m. might be the reversed sequence of the type



$$\begin{array}{cccccc} -CH & -CH_2- & CH_2- & CH & -CH_2- & CH- \\ | & & & | & & | \\ CH_3 & & & CH & & CH_3 \\ & & & \| & & \\ & & & CH_2 & & \end{array}$$

this is analogous to the previous one but a gamma-gauche effect is lacking. This attribution is also consistent with the propene CH peak at 32.53 p.p.m. again the downfield shift might be attributed to the lack of a gamma-gauche effect.

The previous attribution seems to agree with the combined ^1H–^{13}C shifts well observable in the hetero correlated 2D-NMR map (see Fig. 3). In Fig. 3 it can be easily seen that the ^1H shifts corresponding to the previously considered CV resonances lie well into the allyl region of 1.8–2.5 p.p.m. From the above assignments of NMR resonances the following conclusions on the structure of the uPP copolymer can be drawn; a butadiene–propene copolymer exists with 1.5–2.0% of butadiene and such butadiene is present mostly, but not completely, as vinyl. Moreover the 60% of polybutadiene is interdispersed among propene units, the remaining 40% is present as short 1,2 polybutadiene blocks.

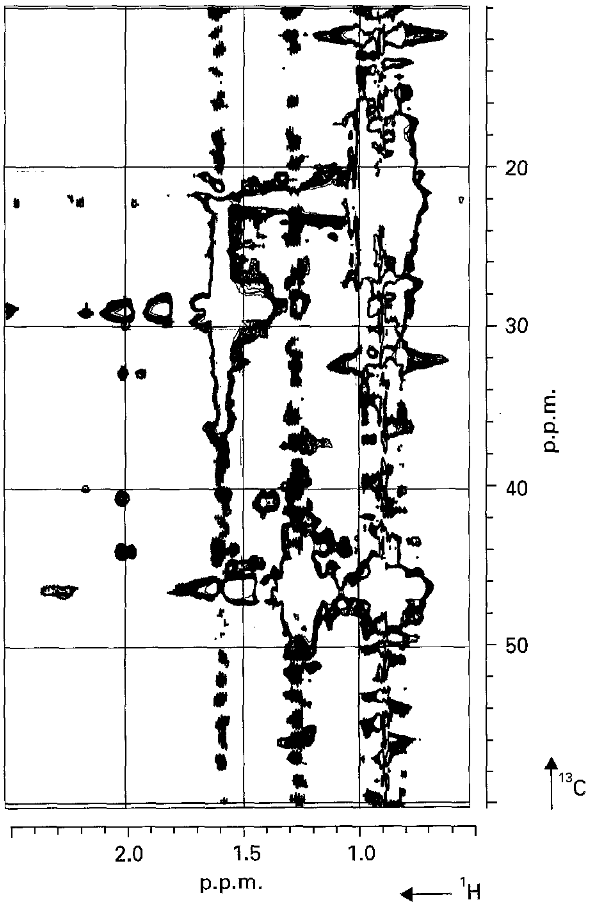
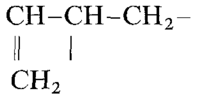


Figure 3 600.13–150.91 MHz ^1H–^{13}C heterocorrelated two-dimensional map. Reverse detection. The dimensions of the two-dimensional matrix are 2K.512 words. Times for a single scan are: 0.3 s acquisition and 1.2 s relaxation delay. 400 scans were allowed for each file, corresponding to 85 h which is the total time for the acquisition of the two-dimensional matrix.

From NMR ^1H spectra of the uPP–g–PS and uPP–g–PMMA copolymers the following molar ratios have been calculated, respectively: moles PS/moles PP are equal to 4/6 and moles PMMA/moles PP are equal to 1/10.

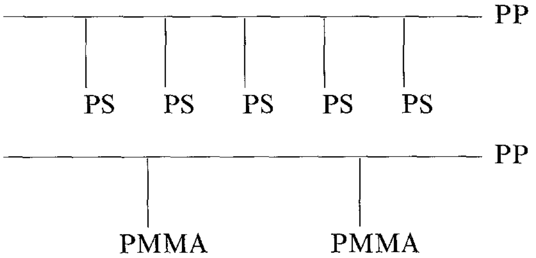
The ^{13}C NMR spectra of uPP–g–PS and uPP–g–PMMA copolymers are shown in Figs 4 and 5, normalized on CH_3 peak. It should be pointed out that the resonance at 113 p.p.m. is to be attributed to CH_2 in the sequences



$$\begin{array}{ccc} CH- & CH- & CH_2- \\ \| & | & \\ CH_2 & & \end{array}$$

in the case of uPP–g–PS copolymer which exhibits an intensity 30% lower than that exhibited by uPP–g–PMMA copolymer. Moreover, the peaks due to CH are split indicating an easy insertion of the styrene (see Fig. 4). The PS is atactic. On the other hand, for uPP–g–PMMA copolymer no points of insertion can be detected (see Fig. 5) indicating that the PMMA is present in long blocks with very few points of insertion. Such findings seem to indicate that only a limited number of active species is available for the graft copolymerization of methylmethacrylate. The PMMA is atactic.

From the above it may be concluded that very different molecular structures are shown by uPP–g–PS and uPP–g–PMMA copolymers, respectively. Such molecular structures can be schematically modelled as follows



3.2. Thermal properties of copolymers as obtained from synthesis process

All the DSC thermograms of samples of the uPP, uPP–g–PMMA and uPP–g–PS copolymers, as obtained from the synthesis process, show a single broad fusion peak when heated from RT to 190 °C (see Fig. 6). Such fusion peaks are to be ascribed (taking into account the results of NMR analysis previously reported) to the melting of the propylenic sequences; the broad peaks indicating irregular and probably thin crystals. The temperature positions of such peaks are reported in Table II together with the crystallinity

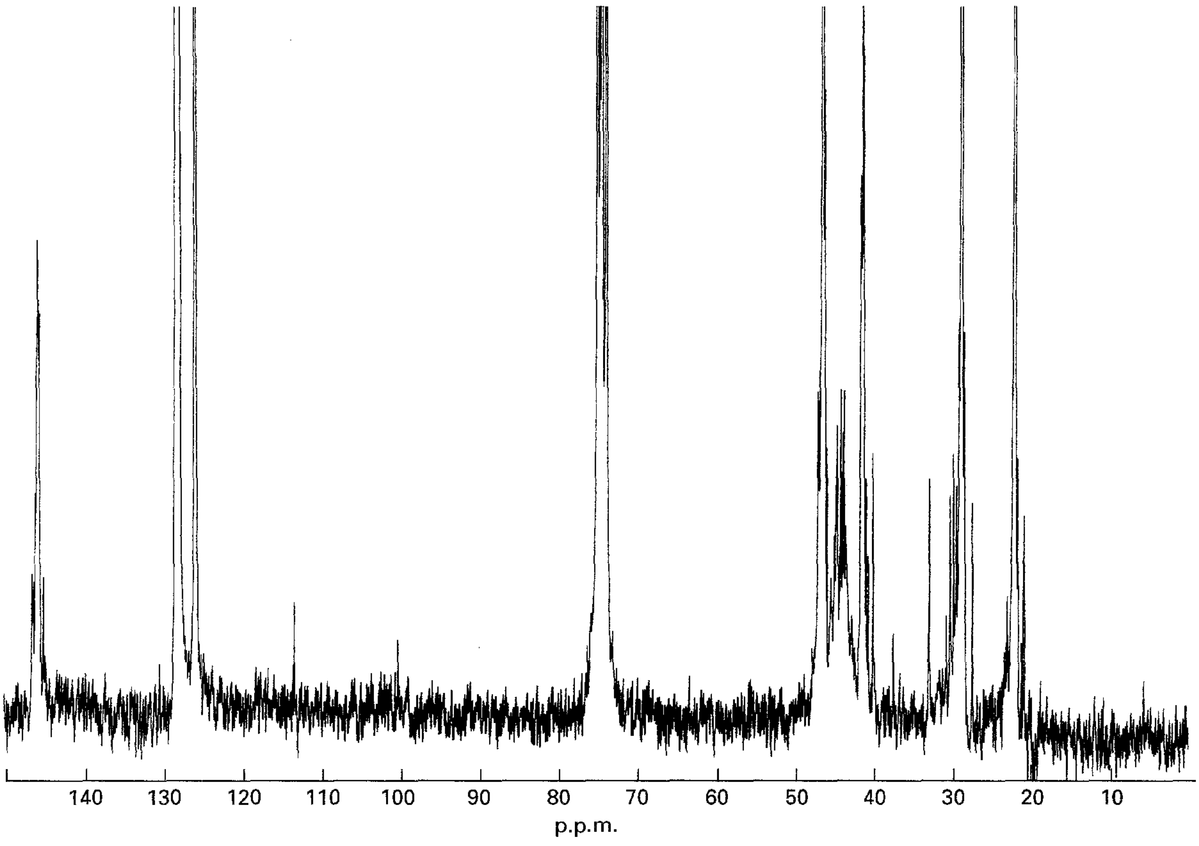


Figure 4 150.91 MHz ^{13}C spectrum of the uPP–g–PS graft copolymer.

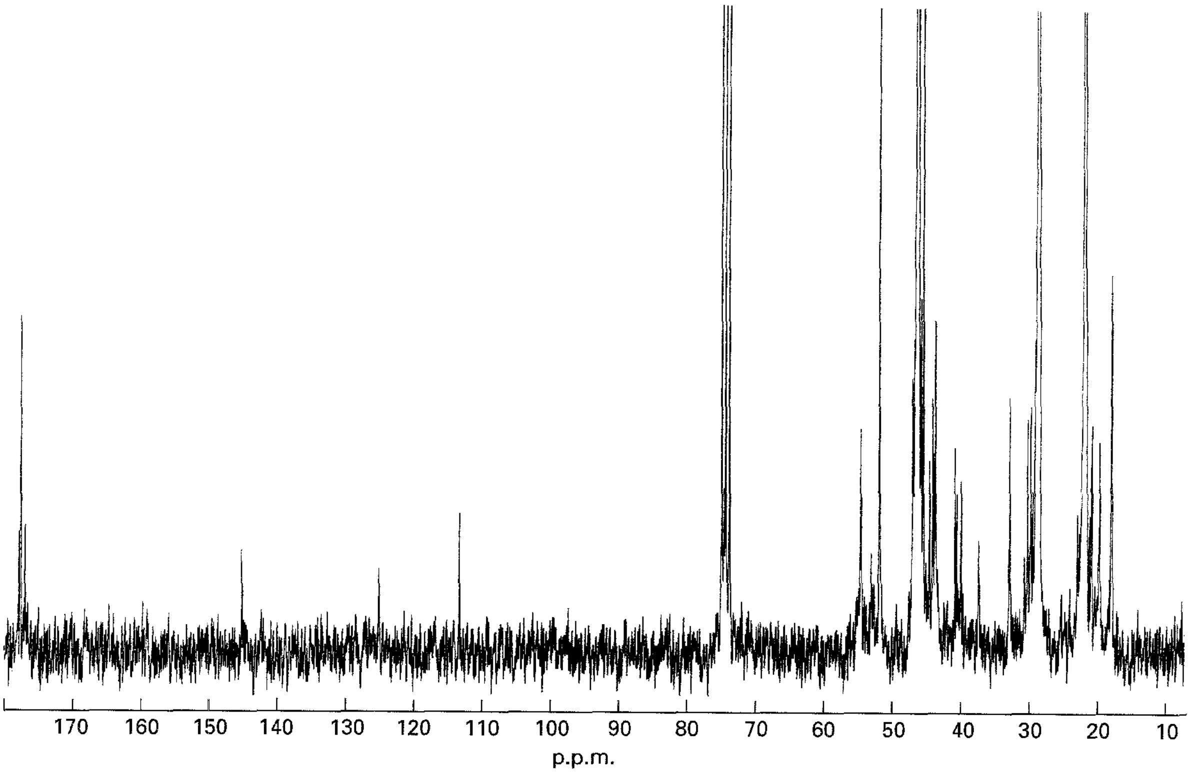


Figure 5 150.91 MHz ^{13}C spectrum of the uPP–g–PMMA graft copolymer.

index (X_c) and the crystallinity index of the uPP phase $X_{c(uPP)}$ As shown in such a table, the same T'_m value of 132 °C is shown by the three copolymers suggesting that the propylenic sequences able to crystallize could have comparable constitutional and configurational regularity, irrespective of molecular structure and composition of the investigated copolymers. uPP and uPP–g–PMMA copolymers exhibit the same X_c value, a comparatively lower X_c value being exhibited by uPP–g–PS copolymer (see Table II). It should

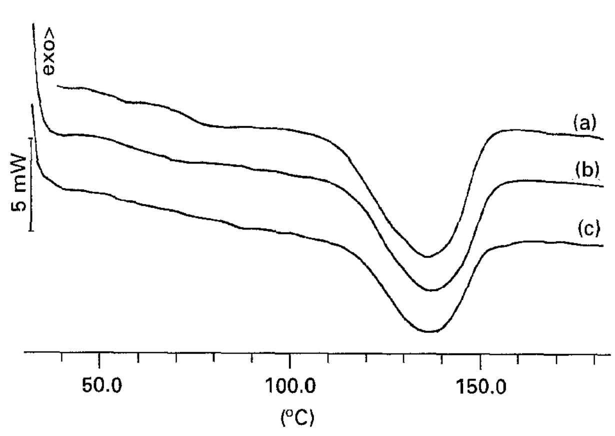


Figure 6 Melting endotherms of uPP (a), uPP–g–PMMA (b) and uPP–g–PS (c) copolymers as obtained from the synthesis process. Heating rate $= 20\,^{\circ}\mathrm{C\,min^{-1}}$.

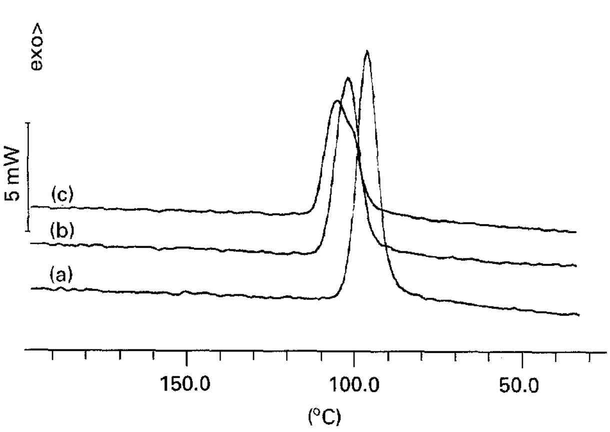


Figure 7 Non-isothermal crystallization curves of uPP (a), uPP–g–PMMA (b) and uPP–g–PS (c) copolymers. Cooling rate $= 10\,^{\circ}\mathrm{C\,min^{-1}}$.

TABLE II Apparent melting temperature (T'_m), crystallinity index (X_c) and crystallinity index of uPP phase (X_c(uPP)) for uPP, uPP–g–PMMA and uPP–g–PS copolymers, as obtained from the synthesis process

Sample	T'_m(°C)	X_c(%)	X_c(uPP) (%)
uPP	132	22	22
uPP–g–PMMA	132	22	27
uPP–g–PS	132	16	24

TABLE III Apparent melting temperature (T'_m), crystallinity index (X_c) and crystallinity index of uPP phase (X_c(uPP)) for sample of uPP, uPP–g–PMMA and uPP–g–PS copolymers, after non-isothermal crystallization

Sample	T'_m(°C)	X_c(%)	X_c(uPP) (%)
uPP	141	25	25
uPP–g–PMMA	143	22	28
uPP–g–PS	139	17	27

be noted, finally, that the $X_{c(uPP)}$ values shown by the graft copolymers were higher than those shown by the uPP copolymer.

3.3. Non isothermal bulk crystallization

The DSC non-isothermal crystallization curves of uPP, uPP–g–PMMA and uPP–g–PS copolymers are shown in Fig. 7. As shown, the uPP copolymer crystallizes between 80 and 107 °C; the temperature position of the maximum of the peak being at 97 °C. It should be noted that the crystallization peaks shown by the uPP–g–PMMA and uPP–g–PS copolymers shift to higher temperatures, the maxima of the peaks being at 103 and 106 °C respectively (see Fig. 7). Such a finding indicates that a faster nucleation process is undergone by the propylenic crystallizable sequences in the graft copolymers. The DSC thermograms of non isothermally crystallized samples of uPP, uPP–g–PMMA and uPP–g–PS copolymers show a single endothermic peak when heated from RT to 190 °C. The temperature position (T'_m) of such peaks, the crystallinity index (X_c) and crystallinity index of uPP phase ($X_{c(uPP)}$) obtained by heating such non-isothermally crystallized samples from RT up to 190 °C are reported in Table III. As shown in Table III, the uPP copolymer exhibits apparent melting temperatures slightly lower and higher than that shown by uPP–g–PMMA and uPP–g–PS graft copolymers, respectively. Moreover, $X_{c(uPP)}$ values higher than those shown by the uPP copolymer are found for uPP–g–PMMA and uPP–g–PS samples. It should be noted that the T'_m and $X_{c(uPP)}$ values shown by the copolymer samples, following a non-isothermal crystallization, are higher than T'_m and $X_{c(uPP)}$ values exhibited by the copolymer samples as obtained from synthesis process (compare Tables II and III).

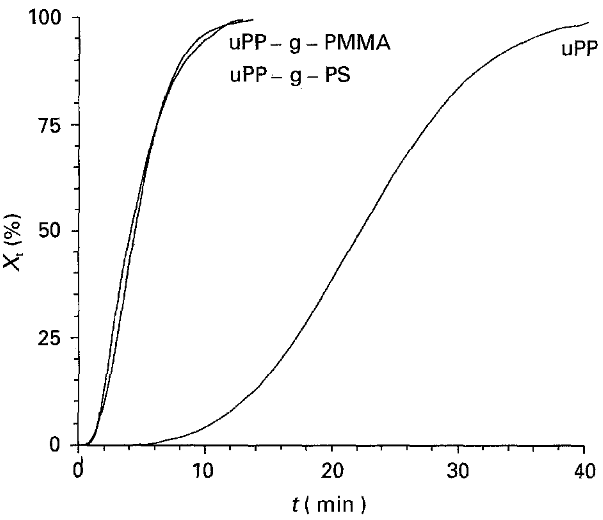


Figure 8 Isothermal crystallization curves of samples of uPP, uPP–g–PMMA and uPP–g–PS copolymers isothermally crystallized at $T_c = 116\,^{\circ}\mathrm{C}$.

3.4. Isothermal bulk crystallization

The kinetics of crystallization from the melt of the uPP, uPP–g–PMMA and uPP–g–PS samples have been studied in the temperature range 112–120 °C. The isothermal curves of crystallization were obtained by plotting, at constant T_c, the crystallized fraction at time $t(X_t)$ against time. A typical crystallization isotherm for each investigated sample is shown in Fig. 8. The variation of the half-time of crystallization ($\tau_{0.5}$), with T_c is shown in Fig. 9. From the examination of

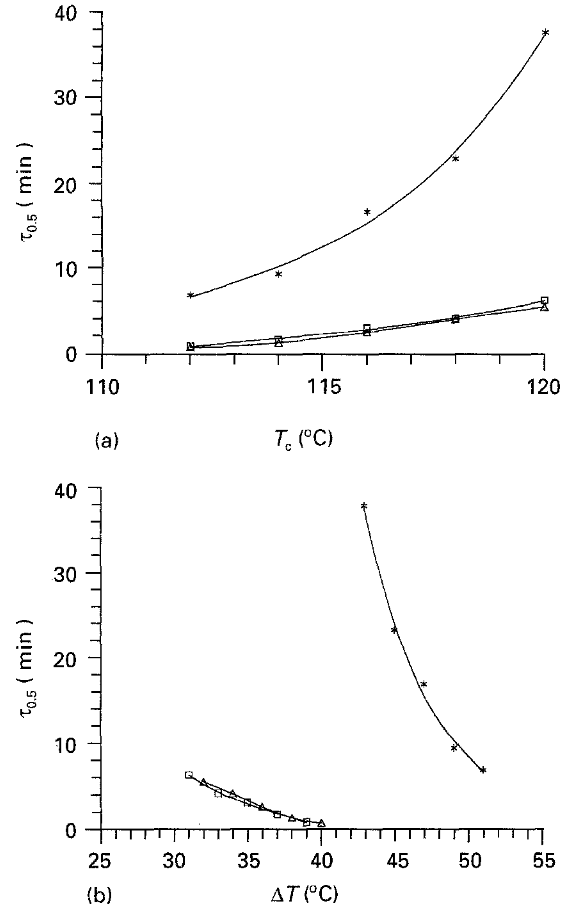


Figure 9 (a) Half-time of crystallization ($\tau_{0.5}$) as a function of isothermal crystallization temperature (T_c) for uPP (*), uPP-g-PMMA (Δ) and uPP-g-PS (□) copolymers. (b) Half-time of crystallization ($\tau_{0.5}$) as a function of undercooling (ΔT) for uPP (*), uPP-g-PMMA (Δ) and uPP-g-PS (□) copolymers.

these trends it emerges that, for a given T_c, the values of $\tau_{0.5}$ exhibited by the graft copolymers are noticeably lower than that shown by uPP copolymer. The extent of such a decrease increases with increasing T_c (see Fig. 9(a)) and that for a given undercooling (Δ_T) the $\tau_{0.5}$ values shown by uPP copolymer are noticeably higher than that shown by uPP-g-PS and uPP-g-PMMA copolymers (see Fig. 9(b)).

The analysis of the kinetics of crystallization for each T_c, has been carried out on the basis of the Avrami equation [18]

$$1 - X_t = \exp(-K_n t^n) \qquad (1)$$

where X_t is the polymer fraction which is crystallized at the time t, $K_n = \ln 2/(\tau_{0.5})^n$, is the kinetic rate constant and n is a parameter depending on the geometry of the growing crystals and on the nucleation process. The values of n and K_n were calculated from the slope and the intercept, respectively, of the straight lines obtained by plotting the quantity log $[-\ln(1 - X_t)]$ against log t (see Fig. 10).

The values of K_n and n for all T_c investigated are reported in Table IV. As shown in this table, n assumes a value of three for uPP copolymer; such a value is in agreement with literature data reported for isotactic polypropylene, indicating that the crystallization process of the copolymer of propylene with butadiene is characterized by a heterogeneous

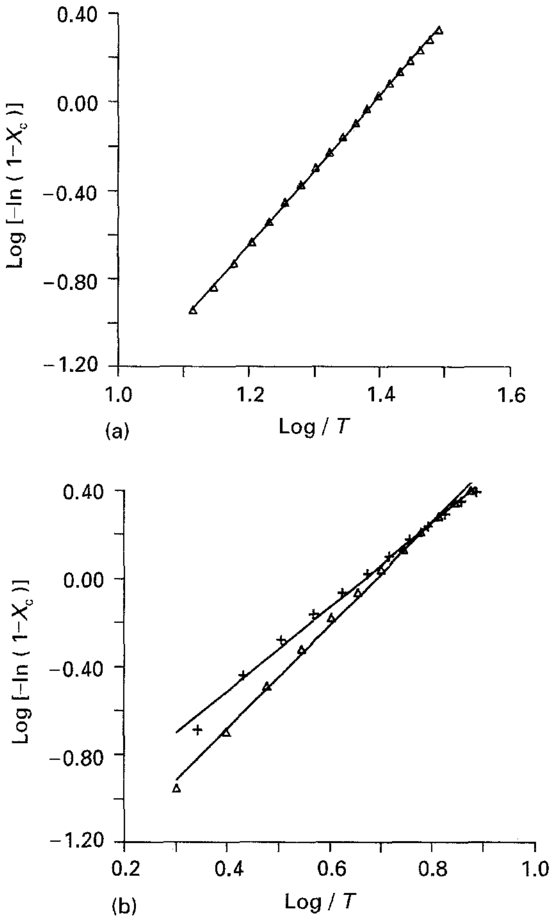


Figure 10 Avrami plots for (a) uPP (Δ) , and (b) uPP-g-PMMA (+) and uPP-g-PS (Δ) copolymers at T_c = 116 °C.

TABLE IV Values of overall kinetic rate constant (K_n) and Avrami index (n) related to all T_c investigated for uPP, upp-g-PMMA and uPP-g-PS copolymers

T_c	uPP		uPP-g-PMMA		uPP-g-PS	
(°C)	K_n	n	K_n	n	K_n	n
112	9×10^{-4}	3.1	0.12	2.6	0.25	2.4
114	2×10^{-4}	3.2	0.07	2.1	0.11	2.0
116	2×10^{-5}	3.4	0.02	2.3	0.05	1.8
118	8×10^{-7}	3.8	0.01	2.1	0.03	1.9
120	3×10^{-7}	3.6	0.002	2.6	0.003	2.5

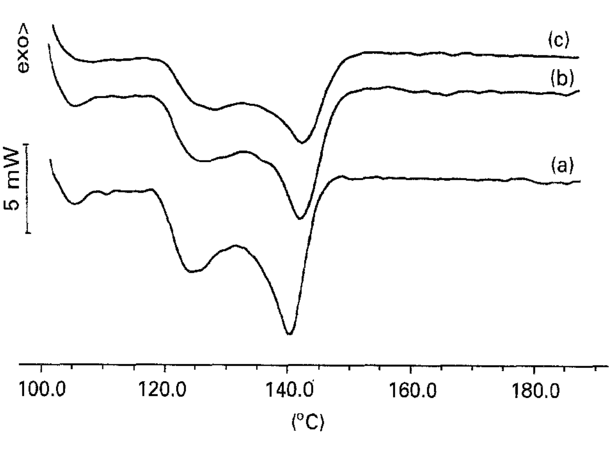


Figure 11 Melting endotherms for samples of uPP (a), uPP-g-PMMA (b) and uPP-g-PS (c) copolymers isothermally crystallized at T_c = 116 °C. Heating rate = 10 °C min^{-1}.

TABLE V Appaarent melting temperature (T'_m) for uPP, uPP–g–PMMA and uPP–g–PS copolymers corresponding to the double fusion peaks (low and high, respectively) as a function of crystallization temperature (T_c)

Sample	T'_m(°C)									
	$T_c = 112$°C		$T_c = 114$°C		$T_c = 116$°C		$T_c = 118$°C		$T_c = 120$°C	
	low	high	low	high	low	high	low	high	low	high
uPP	121	141	123	141	125	141	127	144	130	144
uPP–g–PMMA	123	142	126	144	127	145	127	144	131	144
uPP–g–PS	124	142	124	143	129	143	128	144	131	144

nucleation and by a three-dimensional growth of crystals. It should be pointed out that both graft copolymers, uPP–g–PMMA and uPP–g–PS, show a lower n value (equal to 2) suggesting that the crystallization process of polypropylenic sequences is, on the other hand, characterized by a bidimensional growth of crystals.

TABLE VI The equilibrium melting temperature (T_m) and the morphological factor (γ) for uPP, uPP–g–PMMA and uPP–g–PS copolymers according to the Hoffman–Weeks equation

Sample	γ	T_m(°C)
uPP	2.2	163
uPP–g–PMMA	5.0	151
uPP–g–PS	4.0	152

3.5. Melting behaviour

DSC thermograms of isothermally crystallized uPP, uPP–g–PMMA and uPP–g–PS copolymers show, for all crystallization temperatures investigated, double melting peaks; the first one being broader and lower than the second one (see Fig. 11). The temperature position of such peaks are reported in Table V.

The presence of double fusion peaks can be accounted for by a recrystallization phenomenon occurring during the heating and/or by the melting of crystalline regions with different average degrees of order. Taking into account the NMR results previously reported showing that the distribution of butadiene units is not completely random, it could be hypothesized that comparatively higher T'_m values are to be ascribed to sequences with higher constitutional and configurational regularity.

The melting T'_m values of the lowest peaks are found to increase with T_c, but the straight line obtained by plotting T'_m values versus T_c values for uPP samples show a slope greater than 1. Such a finding does not allow the application of the following Hoffman–Weeks relation [23]

$$T'_m = T_m(\gamma - 1)/\gamma + T_c/\gamma \qquad (2)$$

where T_m is the equilibrium melting temperature and is a constant determined by the ratio between the final thickness of the crystalline lamellae of the spherulites crystallized at T_c after a certain time and the initial critical thickness. The values of T_m are, in fact, calculated by extrapolation of the T'_m versus T_c line to the line $T'_m = T_c$. Therefore the values of T_m and of the morphological factors γ of uPP, uPP–g–PMMA and uPP–g–PS copolymers were calculated by applying the Hoffman–Weeks equation to the melting T'_m values of the highest peaks; such values are reported in Table VI. As shown, for the uPP copolymer T_m is equal to 163 °C; this value is lower than that reported in literature for isotactic polypropylene crystallized from melt [21]. The same T_m value of 163 °C was found by Martuscelli and co-workers [22] for a sample of isotactic polypropylene with 70% mole fraction of isotactic pentads while studying crystallization behaviour of fractions of isotactic polypropylene with different degrees of stereoregularity.

The T_m values found for uPP–g–PMMA and uPP–g–PS graft copolymers are lower than that obtained for uPP copolymer (see Table VI). This could be an indication of higher presence of defects along the crystallizable chain. The high γ values found for such samples seem to support the above results; a large γ, in fact, indicates a more pronounced phenomenon of perfecting of existing crystals following an annealing at the examined T_c. As shown in Table VI, values found for uPP–g–PMMA and uPP–g–PS copolymers are at least twice as high as that shown by uPP copolymer. Moreover, it seems that such γ values tend to increase with increasing the length of the side chains. In fact the highest value is found for uPP–g–PMMA copolymer characterized by comparatively longer blocks and fewer points of insertion.

3.6. Optical microscopy studies

Optical micrographs, taken at crossed polars, of thin films of uPP, uPP–g–PMMA and uPP–g–PS copolymers isothermally crystallized are shown in Fig. 12. As shown, the uPP copolymer crystallizes in a spherulitic superstructure; the size, neatness and regularity of such spherulites slightly increasing with T_c. Note that for a given T_c, the uPP–g–PMMA graft copolymer crystallizes in a spherulitic superstructure comparable to that shown by uPP copolymer (compare Fig. 12(b) with Fig. 12(a)), whereas the uPP–g–PS copolymer crystallizes in microspherulites strongly damaged in neatness and regularity (compare Fig. 12(c) with Fig. 12(a) and (b)). Such a finding could be accounted for by considering the molecular structure of such a copolymer shown by NMR analysis. Owing to their limited number and considerable length the PMMA sequences can be, in fact, easily ejected by the crystal front.

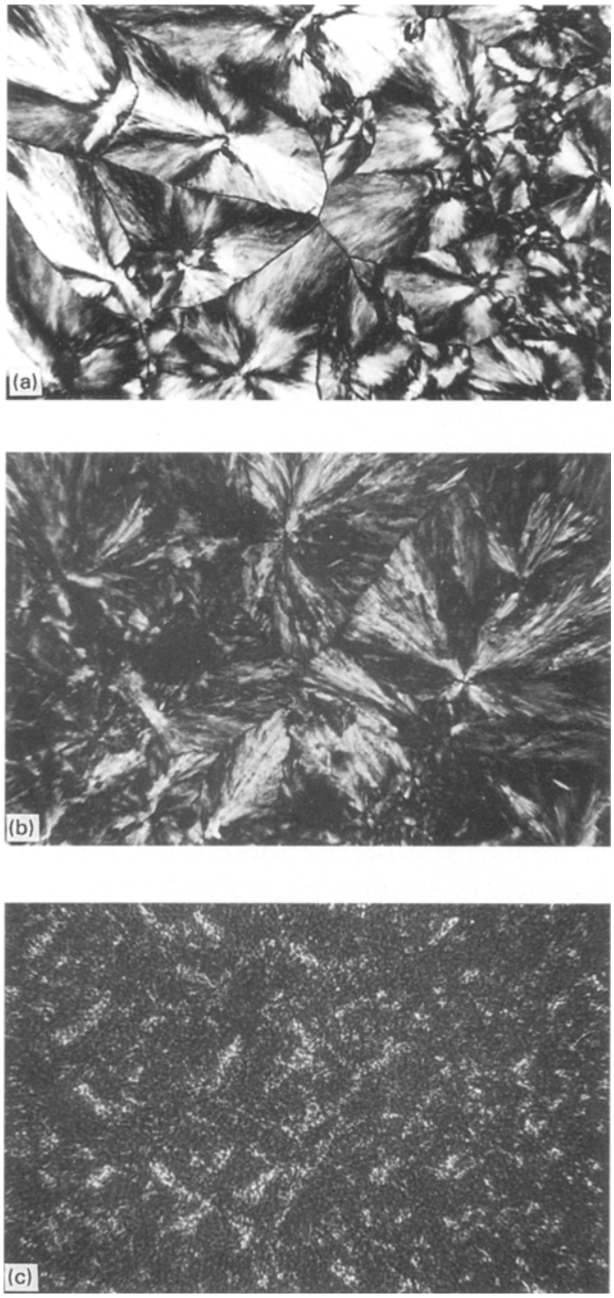


Figure 12 Optical micrographs, taken at crossed polars, of thin films of uPP (a), uPP–g–PMMA (b) and uPP–g–PS (c) copolymers isothermally crystallized at $T_c = 116\,°C$. Magnification is × 540.

TABLE VII Radial growth rate (G) of uPP–g–PMMA and uPP–g–PS copolymers as a function of crystallization temperature (T_c)

	$G(\mu\ min^{-1})$		
Sample	$T_c = 112°C$	$T_c = 116°C$	$T_c = 120°C$
uPP	7.9	4.1	2.1
uPP–g–PMMA	8.2	4.4	2.2
uPP–g–PS	–	–	–

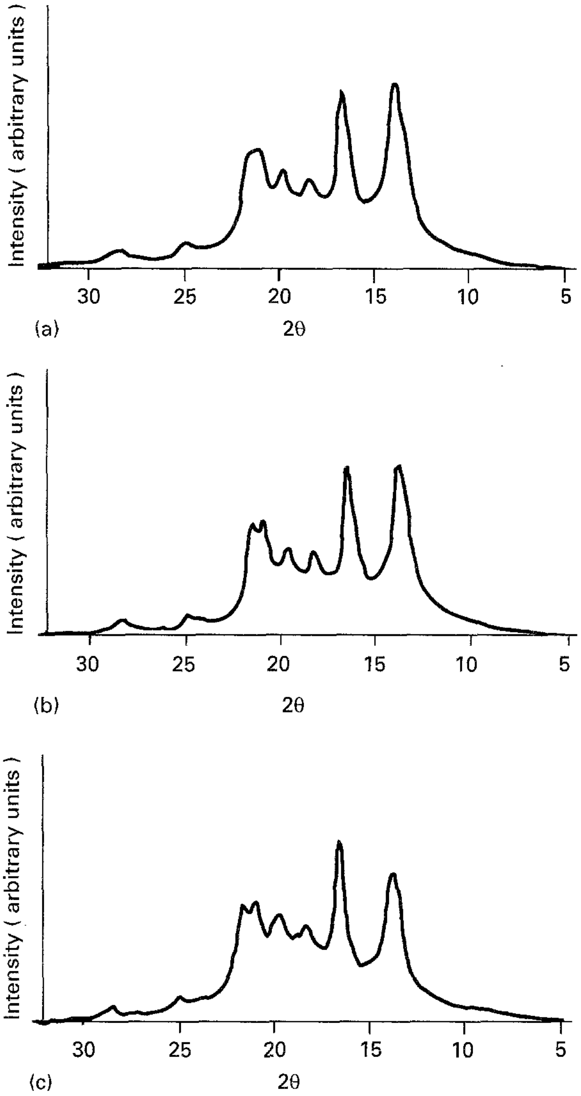


Figure 13 WAXS patterns of samples of uPP (a), uPP–g–PMMA (b) and uPP–g–PS (c) copolymers isothermally crystallized at $T_c = 118\,°C$.

Plots of the radius of uPP and uPP–g–PMMA spherulites against time for all crystallization temperatures investigated give straight lines, indicating that, irrespective of copolymer molecular structure and composition, the concentration of propylenic crystallizable sequences at the growth front is constant during the crystallization process. It should be pointed out, moreover, that for a given T_c, uPP and uPP–g–PMMA copolymers show about the same radial growth rate value, G (see Table VII). Such a finding confirms that no interactions exist between the crystallizable propylenic sequences and the PMMA chains.

No G value can be detected, irrespective of T_c, for uPP–g–PS copolymer. Such a result is to be related to the molecular structure of the uPP–g–PS copolymer and in particular to the distribution of the PS chains shown by NMR analysis. Such PS chains, in fact, owing to the high number and shortness could strongly interfere with the crystallization process of the propylenic sequences.

3.7. Wide angle X-ray scattering studies

Typical WAXS diffractograms of samples of uPP, uPP–g–PMMA and uPP–g–PS copolymers, isothermally crystallized in the range of temperatures investigated, are shown in Fig. 13. As shown, all the three copolymer samples give diffraction peaks whose angles are characteristic for the crystal structure of polypropylene and in addition show a broad diffraction non-crystalline halo. Such a non-crystalline halo is centred at 2θ equal to 17° for uPP copolymer, whereas for uPP–g–PS and uPP–g–PMMA copolymers the halo is shifted toward the value of 2, characteristic of atactic PMMA and PS (14° and 18.5°), respectively [20]. It is to be noted, finally, that no relevant increase of the intensity of crystalline peaks with increasing T_c can be observed. The apparent crystal size (D) of the propylenic sequences perpendicular to the (1 1 0) and (0 4 0) crystallographic planes, as calculated by the Sherrer equation [14], gives results within the range of experimental error with no appreciable differences among the investigated samples. Such results suggest that, for a given T_c, the growth of the crystals of uPP sample is comparable to that shown by the crystals of uPP–g–PMMA and uPP–g–PS samples. The crystallinity indices of the uPP, uPP–g–PMMA and uPP–g–PS copolymers, obtained from the ratio between the areas under the crystalline peaks and the total area, as a function of T_c, are reported in Table VIII. As shown, the trend of such results is quite comparable to that shown by DSC X_c data, also reported in Table VIII for comparison.

3.8. Small angle X-ray scattering studies

Typical Lorentz-corrected desmeared patterns for uPP, uPP–g–PMMA and uPP–g–PS samples crystallized isothermally are shown in Fig. 14. As shown, such desmeared SAXS profiles exhibit defined maxima. By applying Bragg's law, the long period (L), calculated from the peak position, was obtained as a function of T_c. Assuming a two-phase model for the uPP spherulite fibrillae, consisting of alternating parallel crystalline lamellae and amorphous layers, the crystalline lamellar thickness, (L_c) , was calculated using the following relation for the L values.

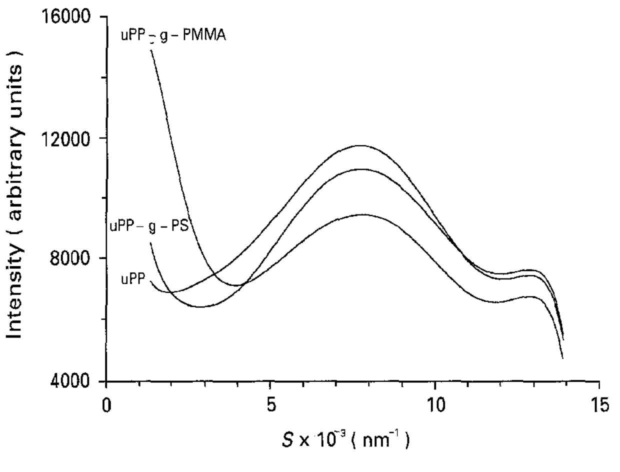


Figure 14 Desmeared SAXS patterns of uPP, uPP–g–PMMA and uPP–g–PS copolymers isothermally crystallized at $T_c = 118$ °C.

$$L_c = \frac{X_c L}{(\rho_c/\rho_a)(1 - X_c) + X_c} \qquad (3)$$

where X_c is the DSC crystallinity index of uPP phase, ρ_c and ρ_a are the densities of crystalline and amorphous phase of isotactic polypropylene (iPP), respectively. The L and L_c values for the three copolymers investigated are reported in Table IX as a function of T_c. As shown by the data reported in this table, for all investigated samples, the increase of L values with increasing T_c is to be considered within the experimental error (50 nm) with no dependence on molecular structure and composition of the copolymer. Comparatively lower L_c values seem to be observed for uPP sample especially at low undercooling (see Table IX).

It is interesting to observe that, plotting the apparent melting temperatures (T'_m) obtained by DSC versus the inverse of lamellar thickness ($1/L_c$) straight lines can be drawn. Therefore, with a certain accuracy the trend of T'_m against $1/L_c$ can be described by the following relation

$$T'_m = T_m - \frac{2\sigma_e T_m}{\Delta H_f}\frac{1}{L_c} \qquad (4)$$

where T'_m is the apparent melting temperature, H_f the enthalpy of fusion of 100% crystalline iPP, L_c the lamellar crystal thickness. According to Equation 4 T_m and σ_e can be respectively determined from the intercept and slope of the straight lines obtained by plotting T'_m against $1/L_c$. The T_m and σ_e values determined by this method are reported in Table X. As shown, the T_m values are comparable to T_m values obtained according to the Hoffman–Weeks equation (compare Tables VI and X). With respect to the free energy of folding, the crystals in the uPP copolymer are characterized by a σ_e of 1.4×10^{-5} J cm^{-2}; such a value agrees with values reported in literature for σ_e of iPP. The σ_e values found for the graft copolymers are much lower than those shown by the uPP copolymer (see Table X) indicating a very much

TABLE VIII Crystallinity index (X_c) values for uPP, uPP–g–PMMA and uPP–g–PS copolymers as a function of T_c, as obtained by DSC and WAXS

T_c (°C)	uPP		uPP–g–PMMA		uPP–g–PS	
	X_c(DSC) (%)	X_c(WAXS) (%)	X_c(DSC) (%)	X_c(WAXS) (%)	X_c(DSC) (%)	X_c(WAXS) (%)
112	29	36	22	30	19	27
114	28	37	26	34	20	29
116	31	35	26	35	21	29
118	31	34	27	36	24	33
120	29	36	28	35	24	33

TABLE IX The long period (L) and the crystalline lamella thickness (L_c) values for uPP, uPP–g–PMMA and uPP–g–PS copolymers as a function of crystallization temperature (T_c)

T_c (°C)	uPP		uPP–g–PMMA		uPP–g–PS	
	L	L_c	L	L_c	L	L_c
112	153	41	152	39	149	43
114	156	41	154	48	154	45
116	155	45	151	47	153	47
118	157	45	156	50	158	54
120	156	45	156	51	156	54

TABLE X The equilibrium melting temperature (T_m) and the free energy of folding (σ_e) of uPP, uPP–g–PMMA and uPP–g–PS copolymers, according to Equation 4

Sample	T_m(°C)	σ_e(J cm^{-2})
uPP	163	1.4×10^{-5}
uPP–g–PMMA	152	6.0×10^{-6}
uPP–g–PS	151	6.1×10^{-6}

irregular and perturbed surface of the crystals. The folding surface free energy can be expressed by the fundamental thermodynamic equation [23]

$$\sigma_e = \Delta H_e - T S_e \qquad (5)$$

where ΔH_e is the folding surface enthalpy and S_e the folding surface entropy. The σ_e variation can be attributed to a variation of the S_e term. Therefore, the observed decrease in σ_e values shown by the graft copolymers is likely to be due to an increase in the S_e term, that is a higher surfacial disorder of lamellar crystals.

4. Concluding remarks

A molecular, structural, morphological and thermal characterization of propylene copolymers containing 3% (wt/wt) of butadiene (uPP) and of uPP modified by grafting polymethylmethacrylate (uPP–g–PMMA) and polystyrene (uPP–g–PS), as synthesized in the Himont scientific laboratories according to Himont patented synthesis methods [1, 5], has been performed using various characterization techniques. Moreover, the influence of concentration, distribution, and type of the uncrystallizable comonomer units on thermal behaviour, structure and morphology of such copolymers and on kinetic, morphological and thermodynamic parameters related to the crystallization process from melt has been examined. The characterization performed on uPP–g–PS and uPP–g–PMMA copolymers will be essential in order to attain the final aim of the research; to study the effects of the addition of such graft copolymers, as compatibilizer agents, in iPP-based blends. In particular, NMR spectroscopy has been used to investigate the molecular structure of such copolymers. The results on the structure of uPP are:

1. a copolymer butadiene–propene exists with 1.5–2% of butadiene; such butadiene is present mostly, but not completely, as vinyl.
2. ~ 40% short 1,2 polybutadiene blocks are present.
3. ~ 60% of polybutadiene is interspersed among propene units. This last result indicates that the distribution of butadiene in the uPP copolymer is not completely random, in fact in a random distribution blocks of 1, 2 butadiene copolymer will not be allowed.

As far as uPP–g–PMMA and uPP–g–PS copolymers are concerned, NMR spectra clearly show that a very different molecular structure is shown by such propylene copolymers. In fact the PMMA is present in long blocks with very few points of insertion, whereas the insertion of the PS is more frequent.

DSC and WAXS experiments showed that both in uPP and in uPP grafter copolymers there are propylenic sequences able to crystallize, even though no relevant increase in X_c values with increasing T_c is found. Optical microscopy revealed that in uPP and uPP–g–PMMA copolymers such propylenic sequences crystallize according to a spherulite morphology. The size, neatness and regularity of such spherulites increase slightly with T_c. A microspherulitic structure is, on the other hand, exhibited, irrespective of T_c, by uPP–g–PS copolymer. Such results have been accounted for by considering the very different molecular structure of the uPP–PMMA and uPP–g–PS copolymers. The few and long PMMA sequences, in fact, are easily ejected out by the crystal front, whereas the PS sequence owing to their high number and shortness can be incorporated in interlamellar and/or interfibrillar regions thus interfering with the crystallization process. It was found, moreover, that in both the grafted copolymers the propylenic crystallizable sequences undergo a nucleation process faster than that undergone by the propylenic sequences in the uPP copolymer. As a matter of fact, the half-times of crystallization shown by the graft copolymers, for a given T_c, are noticeably lower than that shown by the uPP copolymer; the extent of such a decrease increasing with T_c. The analysis of the kinetics of crystallization, carried out on the basis of the Avrami equation revealed that the uPP crystallization process is characterized by a three-dimensional growth of crystals, whereas a bidimensional growth of crystals is found for the uP P–g–PMMA and uPP–g–PS copolymers.

The values of the equilibrium melting temperature (T_m) calculated according to the kinetic theory of polymer crystallization are found in good agreement with the T_m values obtained by plotting the apparent melting temperatures versus the inverse of lamellar thickness by SAXS. The uPP sample shows a T_m value (163 °C) lower than that reported in literature for isotactic polypropylene. Further reduction in such a T_m value is shown by the graft copolymers indicating a comparatively higher presence of defects along the crystallizable sequences. In fact the values of the γ parameter, calculated for such copolymers according to the Hoffman–Weeks equation, are twice as high as that obtained for the uPP copolymer. The free energy of folding of the uPP crystals shows a σ_e value comparable to that reported in literature for isotactic polypropylene. Much lower σ_e values are found, on the other hand, for the graft copolymers confirming a very irregular and perturbed surface of the crystals.

Acknowledgements

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References

1. G. CECCHIN, F. GUGLIELMI and F. ZEREGA, U.S. Patent 4, 602, 077 (1986).
2. G. NATTA and L. PORRI, *Macromol. Chem.* **77** (1964) 126.
3. J. FURUKAWA, *Ang. Makr. Chem.* **23** (1972) 189.
4. N.A. VENEDICTOVA *et al. Polym. Sci. USSR* **27** (1985) 1626.
5. G. CECCHIN and A. DE NICOLA, U.S. Patent 5, 159, 023 (1990).
6. L. D'ORAZIO, C. MANCARELLA and E. MARTUSCELLI, *Polymer* **32** (1991) 1186.
7. L. D'ORAZIO, C. MANCARELLA, E. MARTUSCELLI and G. STICOTTI, *J. Mater. Sci.* **26** (1991) 4033.
8. *Idem., Polymer* **34**, (1993) 3671.
9. *Idem., J. Appl. Polym. Sci.* **53** (1994) 387.
10. A. G. SHAKA, J. KEELER and R. FREEMAN, *J. Magn. Res.* **53** (1983) 313.
11. H. FRIEBOLIN, in "Basic one- and two-dimensional NMR spectroscopy" (VCH, Germany, 1991) p. 192.
12. A. BAX, R. H. GRIFFEY and B. L. HAWKINS, *J. Magn. Res.* **55** (1983) 301.
13. C. G. VONK, *J. Appl. Cryst.* **8** (1975) 340.
14. L. E. ALEXANDER, "X-ray diffraction methods in polymer science" (Wiley–Interscience, New York, 1969).
15. F. CONTI, M. DELFINI, A. L. SEGRE, D. PINI and L. PORRI, *Polymer* **15** (1974) 816.
16. L. P. LINDEMAN and J. C. ADAMANS, *Anal. Chem.* **43** (1971) 1225.
17. A. E. TONELLI in "NMR spectroscopy and polymer microstructure" (VCH, Germany, 1989) p. 54.
18. M. AVRAMI, *J. Chem. Phys.* **7** (1939) 1103.
19. J. D. HOFFMAN and J. J. WEEKS, *Ibid.* **37** (1962) 172.
20. J. W. TURLEY "X-ray diffraction of Polymers" (1965).
21. S. BRANDRUP and E. M. IMMERGUT, "Polymer Handbook" Vol. 5 (Interscience, New York, 1975).
22. E. MARTUSCELLI, M. PRACELLA and L. CRISPINO, *Polymer* **24** (1983) 693.
23. B. WUNDERLICH, "Macromolecular physics" (Academic Press, New York, 1976).

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