ORIGINAL CONTRIBUTION

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Structure development during crystallization of polycaprolactone

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Abstract In this paper, the quiescent crystallization of polycaprolactone (PCL) melts is studied by rheological measurements coupled to calorimetry and optical microscopy. Based on a comparison between the different techniques, we find that the increase in viscoelastic properties during crystallization starts only when a relatively high degree of crystallinity is reached, which corresponds to a much developed crystalline microstructure. Like other semicrystalline thermoplastic polymers, the crystallization of PCL can be seen as a gelation process. In this case, however, we find a peculiar critical gel behavior, as the liquid-to-solid transition takes place at a very high (~20%) relative crystallinity, and this value is independent of temperature. These facts, and the comparison with optical microscopy observations, suggest that the microstructure at the gel point is controlled by the interactions between the growing crystallites. The gel time (from rheometry) and the half-crystallization time [from differential scanning calorimetry (DSC)] both show an Arrhenius-like behavior and have the same pseudoactivation energy. A practical implication of this parallel behavior of t_{gel} and $t_{0.5}$ is that the rheological measurements can be used to extend to higher temperatures the study of crystallization kinetics where DSC is not sufficiently sensitive.

Keywords Crystallization · Gelation · Polycaprolactone

Introduction

In the last decades, the use of rheological techniques in the study of polymer crystallization has gained increasing consensus. Khanna (1989, 1993) was the first to propose rheological techniques to estimate polymer crystallinity and to monitor crystallization kinetics. He pointed out how the evolution of the elastic modulus (as measured at a single frequency) can be related to the evolution of relative crystallinity; a crystallization time can be calculated, and it compares well to those measured by more traditional techniques [such as differential scanning calorimetry (DSC)]. The major drawback of Khanna's works is that the viscoelastic moduli are themselves frequency-dependent. Thus, the crystallization times calculated from viscoelastic measurements are dependent on the selected frequency as well.

More recently, Winter's group showed that the early crystallization stages can be viewed as a physical gelation process (Schwittay et al. 1993). Crystalline order slows down the macromolecular motion and increases the connectivity among molecules. The correlation length diverges

at the critical gel point. During crystallization, a transitional state where the system rheologically behaves as a critical gel is reached; the critical gel point marks the transition between liquid and solid behavior.

Materials at the gel point exhibit a distinctive rheological behavior where the following power law holds for the relaxation modulus $G(t)$:

$$G(t) = St^{-n}; \text{ for } \lambda_0 < t < +\infty \tag{1}$$

where S is the gel stiffness, n is the relaxation exponent, and λ_0 marks the transition to some faster dynamics. The gel Eq. 1 allows for the prediction of all the linear viscoelastic properties. In particular, in the low-frequency region, the viscoelastic moduli are predicted to be power-law functions of the frequency and the loss tangent to be frequency independent. In practice, the following equation can be used to determine the gel point

$$\tan(\delta) = \frac{G''}{G'} = \tan\left(\frac{\pi n}{2}\right) \neq f(\omega); \text{ for } \lambda_0 < t < +\infty \tag{2}$$

where δ is the loss angle. The gel time is detected as the instant when $\tan(\delta)$ is frequency-independent, and the two critical gel parameters (i.e., the stiffness and the relaxation exponent) are calculated from the corresponding viscoelastic data.

For several polyolefins, the critical gel point during bulk crystallization is reached at very low crystallinity (Pogodina and Winter 1998; Horst and Winter 2000; Acierno et al. 2002; Gelfer et al. 2003). Nevertheless, this is not necessarily a general feature of crystallizing polymers which, indeed, can behave in different fashions. Furthermore, at the critical gel point, the local structures are interconnected to form a three-dimensional network, which is presently still not understood. Horst and Winter (2000) proposed three possible types of connectivity at the gel point, and that crystallizing polymers form critical gels of type iii, i.e., the connectivity is provided by amorphous chains immobilized by segments attached to the crystalline structure which interact with similar chains from other structures. Notwithstanding, relations between the local structure and the critical gel parameters are still missing.

In this work, the rheological and morphological evolution during isothermal crystallization of polycaprolactone (PCL) are investigated in parallel. A comparison with other experimental methods, namely, DSC and optical microscopy, allows for a direct correlation between rheology and the evolving microstructure.

Experimental

Materials

For this work, we used a commercial, high-molecular-weight, linear polyester from caprolactone monomer (PCL, CAPA 6800, Solvay). Some relevant properties of the polymer are reported in Table 1. The material has a high crystallinity (~55%), a relatively low melting temperature (~60°C, corresponding to the endothermic peak during the second heating scan at 10°C/min), and a crystallization temperature (defined as the exothermic peak during a cooling scan at −10°C/min) of about 30°C.

Methods

Differential scanning calorimetry analysis was carried out on a DSC2920 (TA Instruments, USA). All DSC measurements were performed under dry nitrogen purge; samples weights were between 3 and 6 mg.

Rheological experiments were performed using a stress-controlled rotational rheometer (SR-200, Rheometric Scientific Inc.) equipped with 25-mm parallel plates and using a gap thickness of 0.5 mm. For the temperature control, a Peltier unit (solid-state heat pump) was used.

Optical observations were made in a Linkam hotstage (CSS450, Linkam Scientific Instruments) by a polarizing microscope (Axioskop 2 Plus, Carl Zeiss Inc.) equipped with a 10× magnification objective. Images were acquired by a color charge-coupled device (CCD) camera (TMC-76S, Pulnix Inc.) and directly digitalized by means of a frame grabber (PCI-1409, National Instruments Corp.). A sample thickness of 0.2 mm was used for optical observations.

The temperature sensors of the rheometer, the calorimeter, and the hotstage were calibrated to minimize temperature differences among the instruments.

Isothermal crystallization experiments were conducted according to the following protocol. After a thermal annealing at 100°C for 5 min, samples were temperature-quenched to the crystallization temperature, T_c, for the isothermal experiments. At T_c, the solidification process was monitored measuring the heat flux, the viscoelastic moduli, or through the optical microscopy.

Table 1 Some relevant properties of the PCL

M_n (g/mol)	M_w (g/mol)	M_w/M_n	T_m (°C)	T_{cryst} (°C)	X_c (%)	T_g (°C)
69,000	120,000	1.74	61	30	55	−60

Results and discussion

Linear viscoelastic characterization of the melt was performed in the temperature range 60–100°C. Time–temperature superposition allows for the reduction of all the data to a single reference temperature. Master curves for the viscoelastic moduli and the complex viscosity, at the reference temperature of 60°C, are reported in Fig. 1. The linear viscoelastic behavior is typical of entangled polymer melts [the critical molecular weight is 5,000 g/mol (Van Krevelen 1972)]. The horizontal shift factor follows an Arrhenius behavior; the activation energy over the universal gas constant, E/R, was found to be 4,650 K. This value is in good agreement with data from the literature (Krishnamoorti and Giannelis 1997).

Differential scanning calorimetry data were collected during isothermal crystallizations at T_c=40, 43, and 45°C. The heat flux data were elaborated to obtain the evolution of relative (mass) crystallinity, α, with time. The as-obtained data are reported in Fig. 2, and they compare well with data from the literature (Madbouly and Ougizawa 2003) obtained on a similar PCL. The Avrami equation, which is often employed for the analysis of crystallization kinetics, can be conveniently written as

$$\alpha(t) = 1 - Exp\left[-\mathrm{ln}(2)\left(\frac{t}{t_{0.5}}\right)^N\right] \qquad (3)$$

where $t_{0.5}$ is the half-crystallization time, and N is the Avrami exponent. Experimental data (at the three TCs) were fitted, with Eq. 3 finding a satisfactory agreement with N=2.5 (independent of temperature) and $t_{0.5}$=389, 1,670, and 3,400 s, respectively. Predictions of the Avrami equation are shown in Fig. 2 as solid lines. The order-of-magnitude decrease of $t_{0.5}$ over just 5°C of temperature change should be noticed as an indication of the high temperature sensitivity of the crystallization.
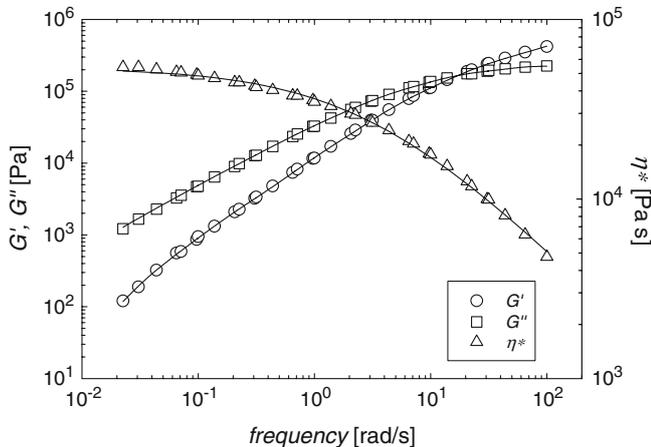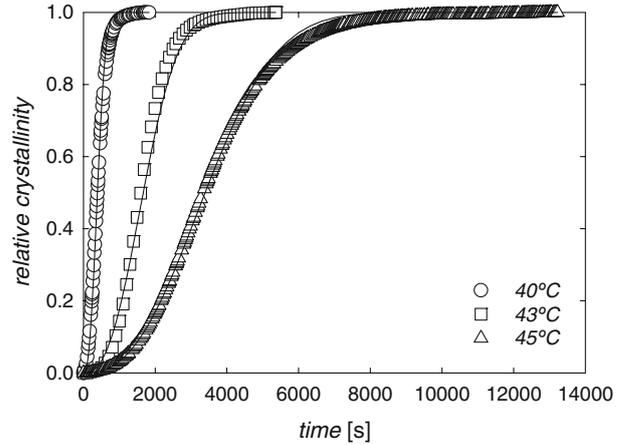

Fig. 2 Relative crystallinity as a function of time during isothermal crystallization at 40, 43, and 45°C. The *solid lines* are predictions of Eq. 3

Parameters $t_{0.5}$ and N allow for prediction of the relative crystallinity evolution at whatever temperature (at least in the range 40–45°C). Therefore, they can be also with the results from rheology and optical microscopy, which were obtained at slightly different temperatures.

When crystallization is monitored by rheological measurements, an increase in the viscoelastic properties during solidification is observed. Typical experimental results are shown in Fig. 3, where the complex modulus (measured at a frequency of 1 rad/s and a stress amplitude of 120 Pa) is plotted as a function of time for an isothermal crystallization experiment at 44.8°C. In Fig. 3, the relative crystallinity evolution at 44.8°C, as calculated using Eq. 3, is also plotted for comparison.

Figure 3 shows that the complex modulus remains constant (at a value corresponding to the supercooled melt) during the first 10^3 s. Afterwards, a relatively fast increase in G^* due to crystallization, is observed. A value of about

Fig. 1 Viscoelastic moduli and complex viscosity as a function of frequency (master curves at the reference temperature of 60°C.)
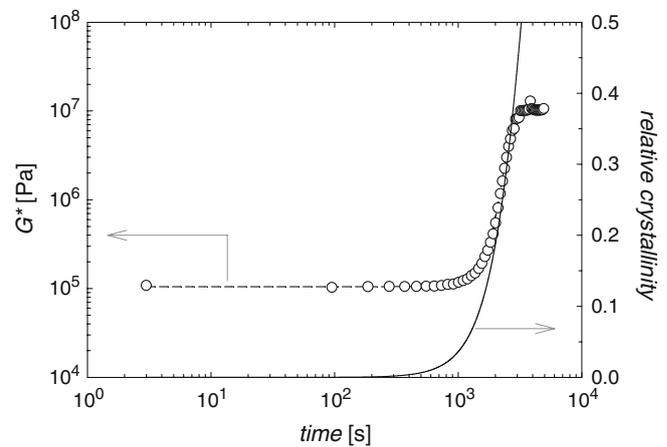

Fig. 3 Complex modulus and relative crystallinity evolution during isothermal crystallization at 44.8°C

10 MPa (typical for a semicrystalline thermoplastic) is reached within 3×10^3 s.

From the comparison of elasticity and crystallinity evolutions, it can be observed that the increase in the complex modulus begins when much crystallinity (more than 10%) has already developed. Furthermore, when G^* reaches the value of 10 MPa, the crystallization is not yet completed, and the relative crystallinity is about 40%. A further increase in G^* when the crystallinity exceeds 40% cannot be appreciated due to the logarithmic scale on the ordinate.

Observations by the polarizing microscope (under the same thermal conditions used for the rheological experiments) were performed to follow the morphological evolution. In Fig. 4, the micrographs taken during crystallization at 44.8°C are shown. A comparison of Figs. 3 and 4 shows again that much crystallinity has already developed when a complex modulus increase becomes detectable. Fig. 4b (which corresponds to the gel point, see further in the text) is a snapshot after 1,655 s; at this point, the crystalline aggregates have already impinged, and the crystalline phase is almost volume-filling.

Figures 3 and 4 suggest that the PCL is liquid-like (and processable) up to crystallinities of 10–20%, and that, when crystallinity has reached about 40%, the modulus hardly increases any further.

More information on the solidification process can be obtained when the time evolution of the dynamic moduli is observed at different frequencies rather than at a single frequency. In this case, frequency sweeps were continuously performed during isothermal crystallization (at T_c=51.7, 50.7, 49.7, and 48.7°C), and gel time, critical stiffness S, and relaxation exponent n were obtained.

As crystallization proceeds, the viscoelastic response of the material changes from liquid-like to solid-like behavior. The critical gel point is detected by means of Eq. 2, i.e., as the instant when tan(δ) is frequency-independent in the low-frequency region.

Polycaprolactone during crystallization shows the typical tan(δ) pattern evolution of a physical gelation process (see Fig. 5, which refers to a crystallization temperature of 50.7°C). During the initial stages, tan(δ) has a negative slope, which is typical of a viscoelastic liquid. In the low-frequency region, the slope increases in time, and it zeroes
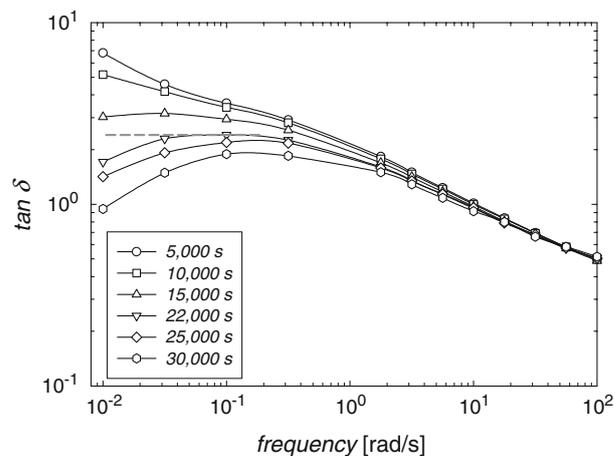

Fig. 5 Evolution of tan(δ) vs frequency during the isothermal crystallization at 50.7°C. The *flat line* indicates the critical gel point

after about 22,000 s, thus indicating a critical gel behavior. As the crystallization proceeds further, the material shows a solid-like behavior with a positively sloped tan(δ) in the low-frequency region.

During the gelation experiments, it was observed that the gel point always takes place when the complex modulus (at a frequency of 1 rad/s) has had a twofold increase with respect to the initial value. This observation allowed to extrapolate the gel time to lower temperatures, where the direct measurement is prohibited by the fast crystallization kinetics.

The gel time and the half-crystallization time are plotted in Fig. 6 as a function of the reciprocal (absolute) temperature. It appears that the gel time is always shorter than the half-crystallization time, but the ratio between the two is constant. This parallel behavior suggests that the (rheological) gel time can be used equivalently to the (DSC) half-crystallization time to describe crystallization kinetics. Rheological crystallization experiments can be used to measure crystallization kinetics at the high temperatures where the DSC measurements are unpracticable due to the low instrument sensitivity. The fact that the ratio $t_{gel}/t_{0.5}$=0.6, independently of the temperature, means that the critical gel behavior is always reached for a relative

Fig. 4 Micrographs taken during isothermal crystallization at 44.8°C. Snapshots at **a** 755 and **b** 1,655 s. The *scale bar* is 100 μm
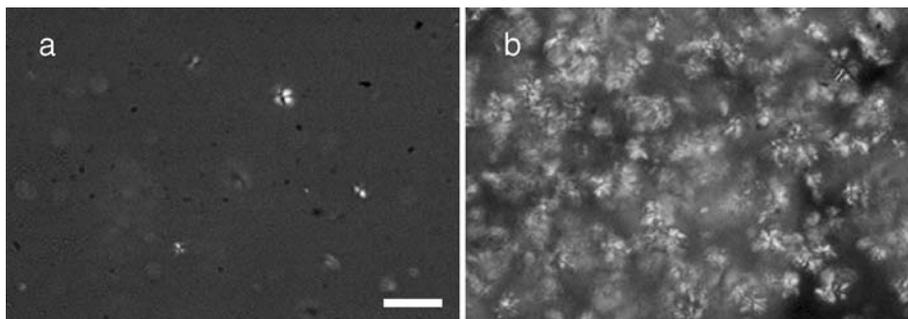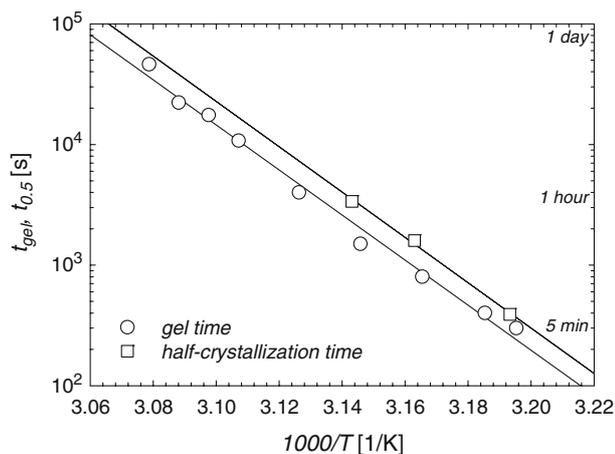
Fig. 6 Gel time and half-crystallization time as a function of reciprocal absolute temperature

Fig. 7 Stiffness and relaxation exponent of the critical gels as a function of temperature. The *solid line* is *S*, as predicted from Eq. 4

crystallinity of (about) 20%. This value is quite high if compared to other systems such as many polyolefins (Pogodina and Winter 1998; Acierno and Grizzuti 2003; Gelfer et al. 2003) and seems to indicate that in the case of PCL, the liquid-to-solid transition is strongly affected by the interactions between growing crystallites. It must be mentioned that other researchers (Boutahar et al. 1998) observed relative large degrees of crystallinity at the solidification threshold. This indicates that the morphological details of the growing microstructure are also important in determining the sol-gel transition. At the moment, however, a definitive and unifying explanation for these phenomena is still missing.

Both gel time and half-crystallization time are Arrhenius-like functions of the temperature, with an average pseudoactivation energy over the universal gas constant, E_c/R, of 43,150 K. Such activation energy implies that the crystallization time scale changes dramatically over the 12°C window explored; t_{gel} is more than 12 h at 52°C and reduces to only 5 min at 40°C.

The thermal behavior of *S* and *n* is reported in Fig. 7. While the stiffness slightly decreases with temperature, the relaxation exponent does slightly increase. The simultaneous decrease of the gel strength and increase in the relaxation exponent is a common feature of many systems showing critical gel behavior and, in particular, of crystallizing polymers. The temperature-variation coefficients of *S* and *n* are in line with observation for other systems (see for example Pogodina and Winter 1998). Conversely, the absolute value of the relaxation exponent ($n_{av}=0.73$) is uncommonly high for a crystallizing system and is comparable with values obtained from unbalanced cross-linking systems (Chambon and Winter 1987) and from low-molecular-weight precursors (Winter and Mours 1997). A temperature dependence of *S* (assuming that
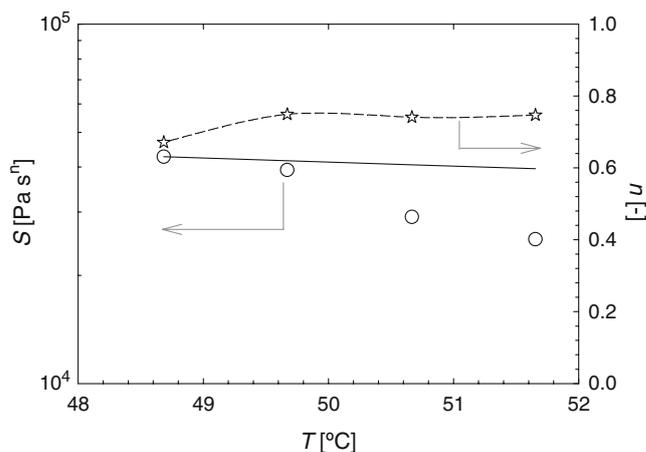
time–temperature superposition holds even for materials at gel point) can be obtained as (Winter and Chambon 1986)

$$S(T) = S(T_r)\frac{a_T^n}{b_T} \tag{4}$$

where T_r is the reference temperature (set to 48.7°C), and a_T and b_T are the horizontal and vertical shift factors of the melt, respectively, as obtained from the linear viscoelastic characterization of the melt. A prediction of Eq. 4 is also plotted in Fig. 7. As we move further from the reference temperature (48.7°C), the discrepancy between experimental data and a prediction of Eq. 4 increases. At higher temperatures, nucleation density decreases, thus producing softer structures at the gel point. This structural information is, of course, not included in Eq. 4, which is an oversimplification of the temperature dependence of *S*.

Conclusions

The crystallization of PCL melts has been studied by calorimetric, optical microscopy, and rheological techniques.

From a comparison of viscoelastic, calorimetric, and optical observations, we found that the viscoelastic properties start to increase at a relatively high degree of crystallinity and when the crystalline structures are very much developed.

Furthermore, PCL showed a critical gel behavior during crystallization, and, differently from many other systems, the liquid-to-solid transition takes place at a high value of relative crystallinity (about 20%), and this value is independent of temperature. These facts, together with morphological observations, suggest that the microstructure at the gel point is governed by the interactions between growing crystallites.

The gel time (from rheometry) and the half-crystallization time (from DSC) both show an Arrhenius-like behavior and have the same pseudoactivation energy, thus meaning that the critical gel behavior is reached at 20% relative crystallinity, independently of the temperature. A practical implication of this parallel behavior of t_{gel} and $t_{0.5}$ is that the rheological measurements can be used to extend to higher temperatures the study of crystallization kinetics where DSC is not sufficiently sensitive.

References

Acierno S, Grizzuti N (2003) Measurements of the rheological behaviour of a crystallizing polymer by an "inverse quenching" technique. J Rheol 47(2):563–576

Acierno S, Grizzuti N, Winter HH (2002) Effects of molecular weight on the isothermal crystallization of poly (1-butene). Macromolecules 35 (13):5043–5048

Boutahar K, Carrot C, Guillet J (1998) Crystallization of polyolefins from rheological measurements relation between the transformed fraction and the dynamic moduli. Macromolecules 31:1921–1929

Chambon F, Winter HH (1987) Linear viscoelasticity at the gel point of a crosslinking PDMS with imbalanced stoichiometry. J Rheol 31(8):683–697

Gelfer M, Horst RH , Winter HH, Heitz Am, Hsu SL (2003) Physical gelation of crystallizing metallocene and Ziegler–Natta ethylene–hexene copolymers. Polymer 44:2363–2371

Horst RH, Winter HH (2000) Stable critical gels of a crystallizing copolymer of ethene and 1-butene. Macromolecules 33(1):130–136

Khanna YP (1989) Estimation of polymer crystallinity by dynamic mechanical techniques. J Appl Polym Sci 37:2719–2726

Khanna YP (1993) Rheological mechanism and overview of nucleated crystallization. Macromolecules 26(14):3343–3639

Krishnamoorti R, Giannelis EP (1997) Rheology of end-tethered polymer layered silicate nanocomposites. Macromolecules 30:4097–4102

Madbouly SA, Ougizawa T (2003) Rheological investigation of shear-induced crystallization of poly(ε-caprolactone). J Macromol Sci Part B B42(2):269–281

Pogodina NV, Winter HH (1998) Polypropylene crystallization as a physical gelation process. Macromolecules 31 (23):8164–8172

Schwittay C, Mours M, Winter HH (1993) Rheological expression of physical gelation in polymers. Faraday Discuss 101:93–104

Van Krevelen DW (1972) Properties of polymers correlation with chemical structure. Elsevier, Amsterdam

Winter HH, Chambon F (1986) Analysis of linear viscoelasticity of a crosslinking polymer at the gel point. J Rheol 30 (2):367–382

Winter HH, Mours M (1997) Rheology of polymers near liquid–solid transitions. Adv Polym Sci 134:165–234