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Rheological evidence of modifications of polypropylene by β-irradiation

Note added in proof This paper is the third in a series concerned with the use of the phase angle vs the dynamic modulus plot, which is also referred to as the "van Gurp-Palmen plot" in the recent literature. In the review process we were notified that its application began before it was taken up by van Gurp and Palmen. Therefore we changed the terminology and henceforth refer to the plot as the "δ vs G_{red} plot".

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Abstract Electron beam irradiation can be used to induce chemical changes in polymers. The resulting reactions lead to both degradation and crosslinking of polymer chains, depending on reaction conditions. In neat polypropylene, degradation dominates and results in a decrease of molecular weight and worsening of mechanical properties. Enhanced crosslinking can be achieved by utilising a polyfunctional monomer. Triallylisocyanurate (TAIC) serves this purpose and can be used to crosslink polypropylene effectively. The corresponding changes of the rheological properties can be observed using oscillatory and creep experiments when changing the amount of TAIC added as well as the absorbed radiation dose. Depending on these parameters, we attribute the rheological properties to chain degradation or formation of a network and gelation. The phase angle vs the dynamic modulus plot is a useful analytical tool for characterisation of the resultant structures. Some samples showed behaviour that leads us to assume broadening of the molecular weight distribution and long chain branching. Resulting from the parameter dependencies, a topological state diagram is proposed to map parameter values to corresponding polymer structures.

Keywords Electron beam radiation · Polypropylene · Crosslinking · Long chain branching · Linear viscoelasticity

Introduction

Ionising radiation can be employed to induce chemical reactions on polymer chains and modify property profiles. Frequently used for this purpose are γ-, β- and UV-radiation. The primary effect of radiation on thermoplastic polymers is creation of macroradicals and ions after scission of bonds (Spinks and Woods 1990). Built radicals lead to further changes in molecular structure through chemical reactions (Dole 1972; Clegg and Collier 1991). The final consequences are branching, crosslinking and degradation of the polymer chain (Charlesby 1960; Chapiro 1962). These processes are in competition and which one predominates depends on the type of the polymer as well as the applied dose, dose rate, type of radiation and temperature (Henglein et al. 1969; Sarcinelli et al. 1997; Spadaro and Valenza 2000).

Depending on particular applications, one of these effects is desired. Crosslinking enhances resistance towards mechanical and thermal stress as well as damage caused by solvents and chemicals. Degradation under mild conditions can be useful for molecular weight reduction (altering the crystallisation behaviour) as well as for narrowing of the molecular weight distribution.

The chemical constitution of a polymer has a strong influence towards its reaction to irradiation. Whereas polyethylene can be readily radiation crosslinked, the substitution of H-Atoms in the polyethylene structure with groups like CH_3, F, Cl or $COOCH_3$ leads to an increase of side reactions and reduces the efficiency of

crosslinking (Henglein et al. 1969). In all polymer structures, crosslinking and degrading reactions will take place concurrently. It is possible to influence the balance between the two by means of parameters such as radiation dose, dose rate and temperature.

At high dose rates, which are common when using electron accelerators as radiation source, degradation of polypropylene is greatly promoted and leads to molecular weight decrease. The macroradicals created during exposition lead to chain fractures due to successive β-scission reactions (Martakis et al. 1994). In order to support crosslinking and reduce chain degradation, enhanced crosslinking can be carried out by utilising a polyfunctional monomer (Benderly and Bernstein 1969; Čapla et al. 1983; Nojiri and Sawasaki 1985; Waldron et al. 1985; Sawasaki and Nojiri 1988; Yoshii et al. 1996). The crosslinking agent has the capability to react with several macroradicals and build links between chains while consuming macroradicals which would otherwise undergo β-scission. The probability of successful crosslinking between chains is thus increased. This lowers the necessary radiation dose, which in turn helps avoid harmful effects of radiation on the material.

It is possible to produce long chain branched polypropylene by electron radiation without additional monomers to acquire high melt strength material. In one study (Rätzsch 1999), it has been shown that the equilibrium between scission and recombination of macroradicals is dependent on temperature. After irradiation in the range of 60–80 °C, long chain branched structures were found. These were defined as such materials that exhibit high melt strength. Thus, melt strength detected by the rheotens method and the moduli detected in oscillatory rheological measurements at low frequencies served as factors for successful long chain branching. To achieve this, two approaches were presented. One is the utilisation of electron beam radiation in an inert atmosphere, while the other makes use of a monomer that can be grafted to the macroradicals and thereby reduce the occurrence of β-scission reactions. Increase of the aforementioned factors were found for these systems. Other methods of characterisation were not considered.

Sarcinelli et al. (1997) have managed to forecast the effects of γ-radiation on molecular structure. They derived a kinetic model for the evolution of double bonds and radical concentrations. This permitted them to predict the dose and dose rate under which a net increase of molecular weight would take place, due to crosslinking outweighing degradation. The existence of inversion conditions was shown as part of the model. Rheological measurements proved the inversion phenomenon, showing that molecular weight increase takes place at high doses and low dose rates. If, on the other hand, the absorbed dose is lower (or the dose rate is higher) than the corresponding value given by the inversion curve, degradation will predominate. The dependence of the dynamic viscosity on shear frequency was applied to determine the dominating process. The results of gel extraction tests were used to confirm the inversion. Samples containing insoluble parts were thus found in the region where branching and crosslinking were suspected, whereas samples below the inversion curve were completely soluble. Quantitative values for gel contents were not given.

Benderly and Bernstein (1969) employed allyl methacrylate as a polyfunctional monomer to crosslink polypropylene using γ-radiation. Copolymers of propylene were also examined. Although no results of oscillatory experiments were shown, they found a decrease in creep compliance at 185 °C with increasing radiation dose. In addition, varying extents of creep decrease resulted from different types of polymer used. Changes in creep behaviour were attributed to differing crosslinking densities. Gel contents were found to be present after irradiation and reached up to 80% and beyond. Mechanical properties were also shown to be adversely affected.

Since large scale application of radiation crosslinking has been possible for 30 years, many studies have been carried out on property modifications in widely used polymeric materials, using ionising radiation. However, few publications have focused on radiation induced changes in rheological properties. The corresponding techniques applicable for evaluation of such structures are well documented. Investigation of radiation modified polymer systems by rheological analysis is thus a worthwhile effort.

It is the aim of this paper to show how polypropylene reacts to electron beam irradiation when the polyfunctional monomer triallylisocyanurate (TAIC) is employed. Rheological data from oscillatory and creep measurements are presented and correlated with quantitative results from gel extraction tests. Insights are presented on how the degree of crosslinking changes, along with rheological behaviour, when radiation dose and quantity of TAIC are altered. The impact of the balance between degradation and crosslinking is shown, as it affects the flow properties of the melt. Probable molecular structures are pointed out and a state diagram is presented to show the necessary parameter values for the attainment of these structures.

Experimental

Materials The isotactic polypropylene used for sample preparation was "Novolen 1100 N" obtained from *Targor*. The molecular weight average (M_w) was approx. 210,000 g/mol and polydispersity (M_w/M_n) was 3.5. Melting point was determined by DSC as 163 °C. The triallylisocyanurate was obtained from *Aldrich*.

Preparation of samples For convenient handling of TAIC, a master batch of polypropylene containing 10 wt% TAIC was prepared using a twin screw extruder *Werner & Pfleiderer* ZSK-25. Temperature was set to 200 °C. Vacuum was not applied due to the

low boiling point of TAIC. Further processing was done to yield material with varying contents of TAIC. For this, the obtained master batch was mixed with more polypropylene and fed into a twin screw extruder *Collin* Teachline ZK-25 at 190 °C. The obtained pellets were used to produce test specimens through injection moulding. The test specimens were irradiated by BGS GmbH, Bruchsal/Germany. Irradiation was done under environmental conditions. Total absorbed dose was varied by running the specimens through the irradiation process a specific number of times. In each run, a radiation dose of 10 or 33 kGy was absorbed. After irradiation, all specimens were annealed at 130 °C for 2 h in vacuum to help reach equilibrium conditions inside the material.

Gel extraction The insoluble fractions in the irradiated samples were determined by solvent extraction. Chipped parts of the material were extracted in boiling xylene for 6 h. The solid parts were separated by filtration, dried at 75 °C and weighed. The gel content is the quotient of insoluble residue mass and original mass of the used sample. This procedure, described in DIN 16892 for polyethylene pipes, is applied to other radiation crosslinked materials as well.

Rheometry After they had absorbed different radiation doses, the rheological properties of the materials were measured in a *Paar Physica* UDS-200 rheometer in parallel plate geometry. Plate diameter was 25 mm. All samples had a uniform thickness of 1 mm. Storage and loss moduli were obtained in oscillatory mode and creep compliances were measured by applying a constant stress of 50 Pa in rotational mode. Seven frequency sweeps were carried out between 0.1 and 100 rad/s at temperatures of 170–230 °C in steps of 10 °C. The obtained curves were shifted to yield a master curve for 190 °C. Creep tests were done at 230 °C and stopped after 15 h.

Results and discussion

A first indication towards differences in the irradiated samples that contained TAIC in comparison to irradiated pure polypropylene was found in the appearance of the material. Figure 1 shows two rows of samples after irradiation using various doses. The material of the upper sequence was produced by adding 5 wt% TAIC during processing. The lower sequence constitutes pure polypropylene samples. Absorbed radiation dose
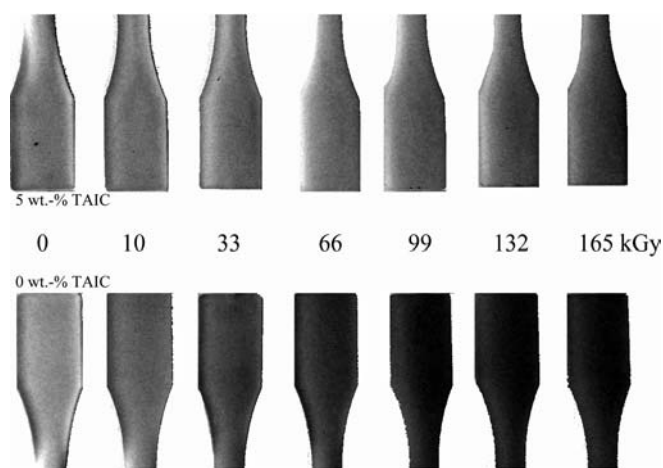

Fig. 1 Appearance of irradiated samples. *Top sequence*: polypropylene containing 5 wt% TAIC; *bottom sequence*: pure polypropylene

increases from left to right. As a result of radiation treatment, yellowing of polypropylene occurs. This is represented in Fig. 1 as grey shades. The amount of discolouration shows in the form of increasingly darker shades with rising absorbed dose. In contrast, material containing TAIC shows very little change in colour, even at high radiation doses. Yellowing can be attributed to chromophores formed. These can be a result from further evolution of macroradicals undergoing chemical reactions. Those reactions may also involve oxygen which diffused into the material from surrounding air. Presumably, the two types of chromophores most responsible for yellowing are carbonyl and hydroperoxide groups (Martakis et al. 1994). The reaction paths leading to these species are likely to cause main chain splits. Therefore, degradation and worsening of mechanical properties are to be expected. In the samples containing TAIC, the created macroradicals are likely to pursue alternative reactions involving the crosslinker and, consequently, chromophores are not formed. Due to the small size of the TAIC molecule, it should have a greater mobility inside the polymer matrix than macroradicals and therefore reactions between TAIC and the latter are facilitated. The TAIC monomer can thus be grafted to the polypropylene chain, retaining its radical property. This new macroradical can react with other polymers. The existence of two more allyl groups on the monomer increases the probability of reaction and raises the degree of crosslinking. Thermogravimetry measurements confirmed that the amount of free TAIC inside the material is lower after irradiation. If enough links between chains are formed, a network structure will result.

To obtain a measure of the degree of crosslinking formed, the gel content can be determined by extracting the sample in hot xylene. For the series of samples not containing any TAIC, the gel content remained at 0%. This was true independently of the applied radiation dose. For samples containing 5 wt% TAIC, gel contents depending on dose are shown in Fig. 2. The values increase with growing dose and reach up to 65% gel. The curve approximates an exponential function of the form $g(d) = g_{max}\left(1 - e^{-(d-d_0)/d_c}\right)$, describing the gel content g in dependence of the dose d. The function approaches a maximum value g_{max} of 64 wt% for high doses. Below a threshold value of about 10 kGy ($d_0 = 9$ kGy), no insoluble parts exist in the sample. The increase of the function with growing dose is described by a characteristic dose d_c of 11 kGy. The obtained dependence is similar to the one found by Nojiri and Sawasaki (1985).

Figure 3 shows the dependence of the storage modulus G′ and the dynamic viscosity η' on the reduced frequency for pure polypropylene irradiated with 10 and 99 kGy as well as non-irradiated material. For each sample, mastercurves are shown that have been obtained by shifting isothermal curves to a temperature of 190 °C. The values for irradiated polypropylene show a decrease
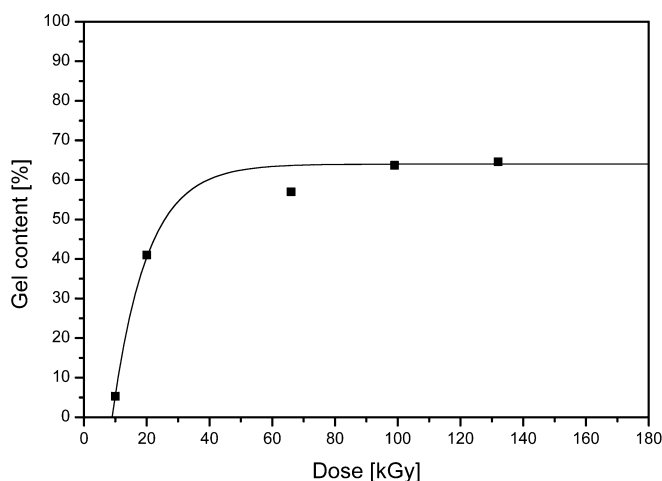
Fig. 2 Dependence of gel content on radiation dose for samples produced with 5 wt% TAIC
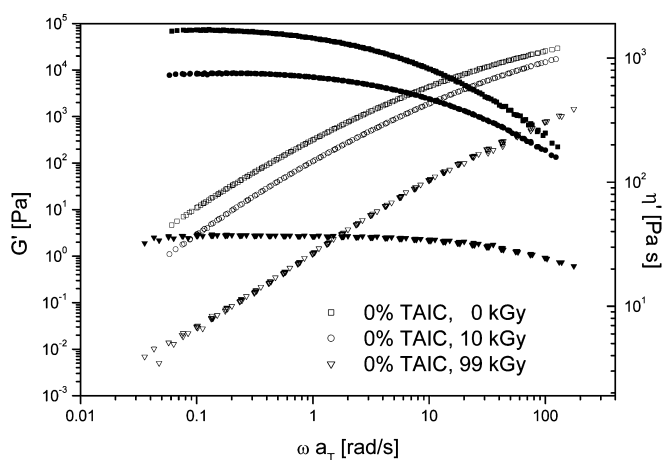

Fig. 3 Storage modulus G′ and dynamic viscosity η′ for pure polypropylene and polypropylene irradiated with 10 and 99 kGy (*open symbols*: G′, *filled symbols*: η′)

of both storage modulus and dynamic viscosity over the entire frequency range. This results from a decrease of molecular weight due to chain scissions. Accordingly, these degradation reactions must have taken place to a considerable extent.

For low frequencies, the zero shear viscosity is reached at 1682 Pa.s in non-irradiated polypropylene ($M_w = 210,000$ g/mol). Radiation treatment leads to a decrease of the zero shear viscosity. The molecular weights can be calculated from these values using the scaling relationship

$$\eta_0 = k \cdot M_w^\alpha. \tag{1}$$

This results in the following equation if the ratio between η_0 values for two different radiation doses $d1$ and $d2$ is considered:

$$M_{w,d2} = M_{w,d1} \left(\frac{\eta_{0,d2}}{\eta_{0,d1}} \right)^{\frac{1}{\alpha}}. \tag{2}$$

The parameter k is a temperature dependent and polymer specific constant. For α, a value of 3.52 was used for isotactic polypropylene with a molecular weight beyond the critical molecular weight M_c (Eckstein et al. 1997). The results are given in Table 1.

The plot in Fig. 4 shows the dependence of the phase angle ($\delta = \arctan G''/G'$) on the reduced complex dynamic modulus ($G_{red} = |G^*|/G_N^0$) for the same series. All three curves are superimposed. The only significant difference is an extension toward higher loss angle and lower modulus values, which is found for increasing radiation doses. This shows once more that the terminal flow region (represented by 90°) is more easily reached after irradiation. From the fact that these curves are mere extensions of each other, without any change in shape, we conclude that there is no significant change in polydispersity or topology with absorbed dose (Trinkle and Friedrich 2001). The polydispersity amounts to approximately 3.5.

Samples produced with 5 wt% TAIC show the storage modulus, in dependence on reduced frequency, depicted in Fig. 5. They exhibit greatly altered behaviour after irradiation. Values for five different radiation doses are shown, together with non-irradiated material. In contrast to samples without polyfunctional monomer,

Table 1 Estimated molecular weights for irradiated polypropylene

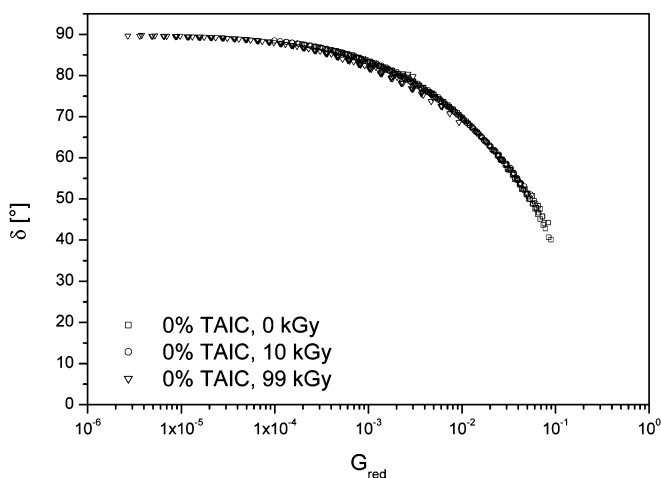| Dose [kGy]	η [Pa s]	M_w [g/mol]
0	1660	210,000
10	750	170,000
99	37	70,000

Fig. 4 δ vs G_{red} plots for pure polypropylene and polypropylene irradiated with 10 and 99 kGy
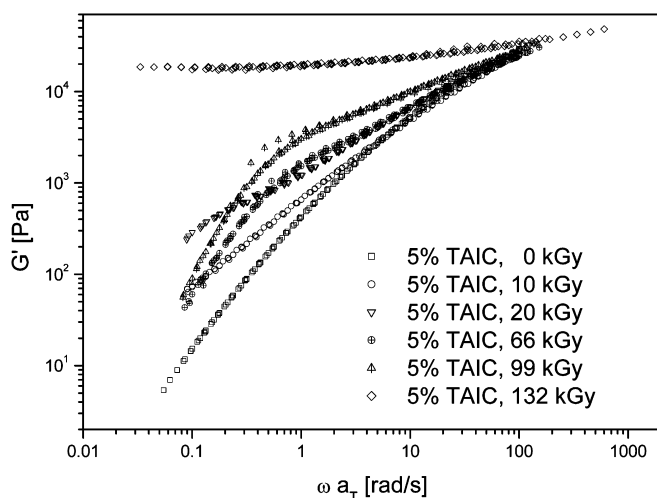
Fig. 5 Storage modulus G′ for polypropylene produced with 5 wt% TAIC and irradiated with various doses

the storage modulus is generally shifted to higher values over the entire frequency range. The difference grows with increasing radiation dose. The data for the non-irradiated sample (containing TAIC) relate in the following way to those of pure polypropylene (see Fig. 3). The values for polypropylene with TAIC in Fig. 5 are slightly lower than those for pure material in Fig. 3 but the two curves are parallel to each other (not shown). This effect is attributed to the presence of TAIC which should be present, at this stage, as a free molecule. Therefore, dilution of the polymer is assumed to be the cause. The slope at the low frequency end is 1.71, corresponding to the value for pure polypropylene.

Setting the absorbed radiation dose to 10 kGy leads to higher values in the low frequency region, resulting in a flatter curve. The slope becomes 0.9. An increase to 20 kGy yields the same effects to a higher extent. The slope falls to 0.65. This means a considerable increase of the terminal relaxation time in both cases, when higher doses are applied. In spite of this, the gel content of the 10 kGy sample was only 5.3%. It is likely that mostly long chain branched molecules exist, which are still soluble. The further increase of the terminal relaxation time in the 20 kGy sample could consequently be attributed to a higher amount of long chain branching in this sample. After absorption of 66 kGy and 99 kGy, the samples show very different behaviour. Although the storage modulus shows further increase in the high frequency region, the flow region is reached sooner, such that the modulus is much lower for low frequencies. The terminal relaxation time decreases again for these samples. As will be shown later, the corresponding structure can be described as a microgel – crosslinked individual domains or particles that are not attached to each other. Irradiation with even higher doses leads to the rheological behaviour shown for the 132 kGy sample.

The slopes decrease to develop into a plateau region with constant modulus for low shear frequencies. The terminal relaxation times increase again and become infinite. Towards high frequencies, a small increase of G′ is still observed. The gel content amounts to 65%. Networks are being formed as a result of crosslinking reactions taking place after creation of macroradicals. The plateau in the curve lets us assume continuous networks which reach the dimensions of the entire sample, resulting in a rubber-like structure.

Plots of the phase angle vs the dynamic modulus corresponding to these mastercurves are displayed in Fig. 6. The accessible data range has been extended using the results of creep measurements to attain results for very long relaxation times. The corresponding creep compliances were used to calculate the retardation time spectra, from which a mastercurve was then computed. The transition area between two analogous curves is not very smooth. This is due to the values for small creep times being experimentally not very reliable. In addition, we can expect the material to be rather inhomogeneous in composition, since the employed polypropylene is a commercial product and also there is a considerable range of chemical reactions that are conceivable involving reactive radical species and a trifunctional monomer. These inhomogeneities could lead to the observed discrepancies, whereas the method generally yields good matches for linear polymers (see Fig. 1 in Trinkle and Friedrich 2001). Nevertheless, the conversion of the creep compliance to an extended δ vs G_{red} plot towards the left side is valuable for the description of the general behaviour for samples irradiated with low doses. As will be discussed, the analysis of the plot is in part based on the appearance of a minimum representing an additional relaxation process. For some samples,
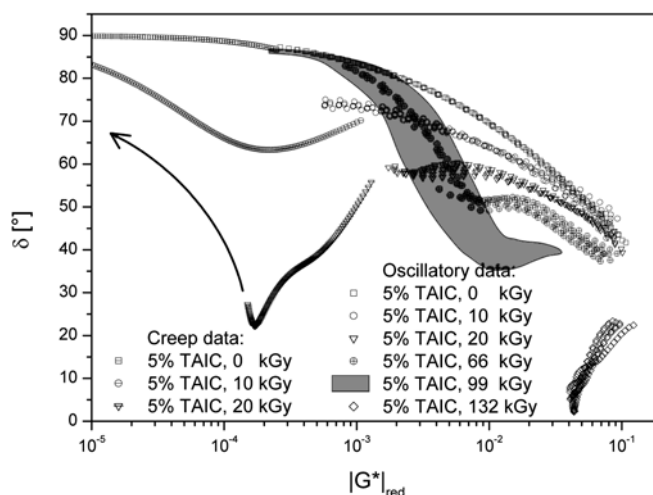

Fig. 6 δ vs G_{red} plots for polypropylene produced with 5 wt% TAIC and irradiated with various doses

this minimum is inside the time range of the creep data. Although the transition between the two data sets agrees only approximately, the minimum itself is a true part of the completed curve.

Whereas the data of the non-irradiated material shows the typical shape of a linear polymer, deviations are found for the other samples. The shown curves can be divided up into four groups. The first group merely contains the unmodified polypropylene. In the second group, consisting of samples irradiated with 10 and 20 kGy, we find that the flow state is not reached inside the oscillatory experimental range. The extended data from the creep experiment shows that, at least for the 10 kGy sample, flow is ultimately attained. For the 20 kGy sample, the available data is limited, but the loss angle δ will presumably also reach 90° eventually, as indicated by the arrow. Both curves in this group show a pronounced local minimum at a reduced modulus of 1.7×10^{-4}. This suggests the existence of two well separated relaxation processes. While the terminal relaxation time is associated with the dynamics of the whole molecule, the second process is accredited to the relaxation of branches (Trinkle et al. 2002). The terminal relaxation time of this polymer is much longer, compared to the relaxation time of linear chains, which can be concluded from the mastercurves in Fig. 5. The curve shapes of the δ vs G_{red} plots agree well with those found by Trinkle et al. for mixtures of long chain branched polymers with linears. We thus assume a mixture of a small amount of long chain branched molecules with longer relaxation time embedded in a matrix of linear species. The higher dose of 20 kGy leads to increased elasticity, represented by a minimum located at a lower loss angle.

A third group includes the samples that have absorbed 66 and 99 kGy of radiation. The 99 kGy curve is more complex and will be discussed separately (see Fig. 7). Its location relative to the other data is marked by the grey area. In these materials, flowing is reached at much higher reduced moduli than in the former group of samples. They are more comparable to neat polypropylene. However, a minimum (now a shallow one, which we call a bump) is also visible in the curve, within the relaxation times that are accessible in oscillatory measurements. With increasing dose, this bump moves downwards to smaller angles and to the right to higher reduced moduli. The bump again represents an additional relaxation process, now of polymers of different topology. The much higher concentration of macroradicals that is expected for this group lets us assume a more highly crosslinked material. It is plausible to assume a higher amount of arms but a decreased arm length, due to the many branch points. The relaxation time of these newly formed species also decreases, compared to the former group (see Fig. 5). A higher branching density (enhanced gel content) together with decreased terminal relaxation time suggest the formation
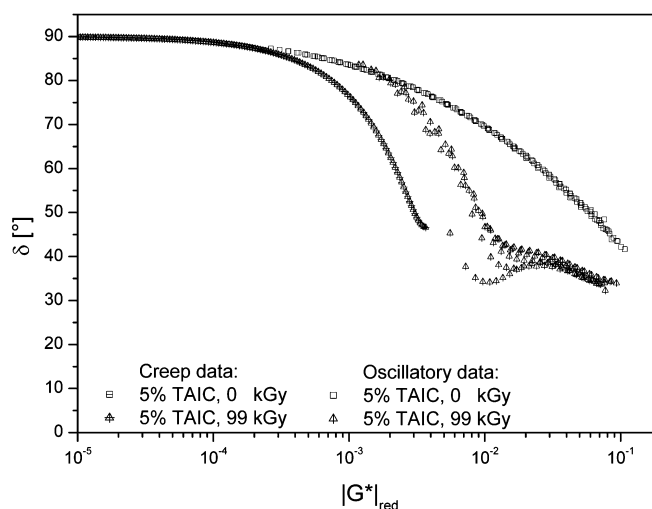

Fig. 7 δ vs G_{red} plots for polypropylene produced with 5 wt% TAIC and irradiated with 99 kGy, compared to pure polypropylene

of microgel structures. In this set-up, locally crosslinked particles that are not attached to one another are dispersed in a matrix of linear polymer chains. Increased radiation doses bring about a transition from molecules with long branches to more densely crosslinked particles with shorter arms. This causes the observed bump in the δ vs G_{red} plot to move in the way described above. Viscoelastic response of specially prepared microgels that resembles the behaviour of our curve, including a terminal relaxation zone, was published before (Antonietti et al. 1995; Pakula et al. 1996) and supports our hypothesis of microgel formation.

Figure 7 shows the curve of the 99 kGy sample, compared to untreated polypropylene. The data derived from oscillatory measurements show a fraction of data points that are shifted to lower values of modulus and loss angle. The oscillatory measurements from which the data was obtained were conducted at temperatures ranging from 170 to 230 °C. For higher temperatures, the time-temperature superposition principle seems to hold true no longer. The deviating data points correspond to a temperature of 230 °C. The extension of the curve for low frequencies was derived from a creep experiment, also conducted at 230 °C. This explains the difference between the extension curve (derived from creep data) and most of the oscillatory data. This results in the grey area in Fig. 6.

Finally, the fourth group comprises all samples that have been irradiated with 132 kGy and more. As the mastercurve has already shown, the material shows the behaviour of an elastic network throughout the accessible frequency range. Creep data also showed an equilibrium creep compliance that was nearly constant, even after 15 h. In the δ vs G_{red} plot, the data stays at the

lower right corner, at a consistently high reduced modulus and a low loss ratio.

The division of the samples into four groups is based, among other things (such as the shape of the δ vs G_{red} plots and the gel contents), on the change of the terminal relaxation time τ, when polypropylene is radiation crosslinked. At low radiation doses, there is an increase of τ, along with a rising absorbed dose. At some point between 20 and 66 kGy, a maximum value for τ is probably passed, after which there is a decrease. This is the domain of the microgel particles. More radiation leads to a higher branching density and shorter arm lengths. Near 66 kGy the minimal terminal relaxation time is crossed. Beyond that point, the microgel areas should be growing until they develop into a continuous single network gel that shows rubber elasticity at 132 kGy.

The same experiments discussed so far were conducted on a series of other polypropylene materials as well. They only differed in the amount of TAIC that was added before radiation treatment. Samples were produced using 2.5 wt% and 1 wt% TAIC. Similar effects were observed as in the samples with 5 wt% TAIC. All polymers obtained after irradiation can be grouped into the aforementioned four categories, depending on the structural effect created by the radiation induced reactions and detected by rheological techniques. The effects depend on the ratio between crosslinking and degradation. This, in turn, can be controlled by adjusting the amount of polyfunctional monomer added and the radiation dose applied. If very little or no monomer is added to the material, radiation exposure will lead to chain degradation and molecular weight decrease. These samples can be combined to form group 1. The remaining three groups have been discussed earlier. If TAIC content and/or radiation dose are low, crosslinking begins to occur and long chain branched molecules result that are not big enough to be insoluble. If TAIC amounts and radiation dose are moderate, crosslinking may predominate, but its extent is not high enough to create a continuous network. The resulting material consists of a microgel with crosslinked domains that are spatially limited, inside a linear matrix. Finally, if both radiation dose and concentration of TAIC are very high, a complete network will be formed and the resulting material will be rubber-like.

To gain an overview of the various effects in dependence of the two parameters "TAIC concentration" and
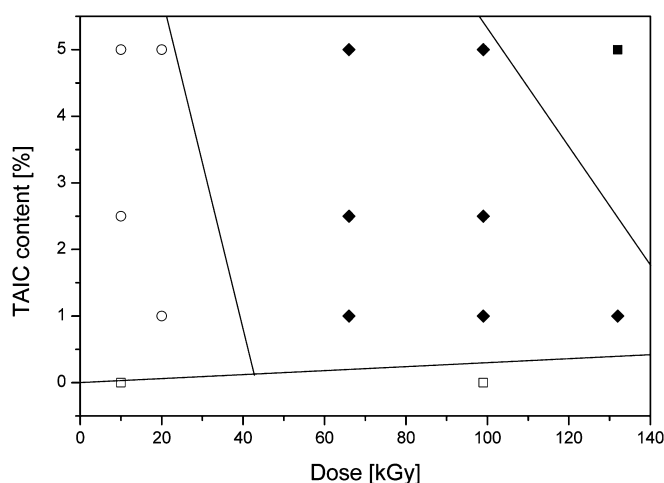

Fig. 8 Classification of all samples into structural categories and the parameter values needed for their attainment. Predominant effects: *open squares*: chain degradation; *open circles*: long chain branching; *filled diamonds*: crosslinking (microgel); *filled squares*: continuous network (gel)

"radiation dose", Fig. 8 presents the interpretations of the rheological data similarly to a phase diagram. The parameter range leading to a certain structure is marked as a two-dimensional area. The lines represent transitions between different states of crosslinking or degradation. However, the transitions are smooth and it is not realistic to give their exact locations. The borders are merely used as rough guidelines to indicate where the transition areas are suspected. Each symbol represents one sample for which rheological data and gel extraction results were evaluated. The respective effect which is assumed as predominant for the sample is given by the type of its symbol. Table 2 summarises the characteristics of the different structural categories, as they were found in the samples.

Conclusions

Electron beam irradiation was successfully used to alter the molecular structure of polypropylene. Pure polypropylene samples were primarily damaged by radiation, due to molecular degradation, causing decrease of molecular weight, yellowing and a more brittle material. The utilisation of the polyfunctional monomer TAIC as a crosslinking agent leads to altered behaviour after

Table 2 Attributes of the structural categories, found in the samples

Category	Symbol	Terminal relaxation time	Bump (δ G_{red} plot)	Gel content
Degradation	Open square	Low	–	0
LCB	Open circle	High	Strong	Low
Microgel	Filled diamond	Low	Weak	High
Network	Filled square	Infinite	–	Maximum

irradiation. Evidence of this was found in the form of insoluble gel contents in the samples, as well as an increase of terminal relaxation times in oscillatory experiments. Low doses presumably lead to long chain branched structures, showing only a small difference in gel contents but a large difference in the slope of the storage modulus. Additional relaxation processes were observed in δ vs G_{red} plots. These processes were either attributed to long chain branched molecules or microgel formation. Higher doses led to samples with a greater gel content but the terminal relaxation time dropped again. With increasing dose, the bump in the δ vs G_{red} plot moved downwards and to the right, representing a change in topology towards a locally crosslinked material that exists within a linear polymer matrix. With even higher absorbed doses, terminal relaxation time ultimately reached infinity. At this point, the rubber-like behaviour is best explained by the assumption of a continuous molecular network.

In the irradiated system there is always a balance between crosslinking and degradation reactions. The molecular structure is a result of these influences. A state diagram was presented to show how four different structural classes could be achieved by selection of the parameters "radiation dose" and "monomer content". Long chain branched structures are the primary consequence of low radiation doses and TAIC contents. The transition to microgels occurs when the radiation dose is raised. It occurs sooner if the TAIC content is higher. Continuous networks will only be formed if both parameters are high enough.

Finally, we conclude that radiation crosslinking of polypropylene in the presence of a crosslinker molecule (TAIC) is an effective way to produce material of diverse molecular topology. Linear viscoelastic measurements together with the determination of gel content are a sensitive method to detect these structures.

References

Antonietti M, Pakula T, Bremser W (1995) Rheology of small spherical polystyrene microgels: a direct proof for a new transport mechanism in bulk polymers besides reptation. Macromolecules 28:4227–4233

Benderly AA, Bernstein BS (1969) Radiation-crosslinked polypropylene: physical and dielectric properties. J Appl Polym Sci 13:505–517

Čapla M, Lazár M, Pajchortová A (1983) Influence of polyfunctional monomers on crosslinking of polypropylene. Chem zvesti 37:561–566

Chapiro A (1962) Radiation chemistry of polymeric systems. Wiley, London

Charlesby A (1960) Atomic radiation and polymers. Pergamon Press, Oxford

Clegg DW, Collier AA (1991) Irradiation effects on polymers. Elsevier, London

Dole M (1972) The radiation chemistry of macromolecules. Academic Press, New York

Eckstein A, Friedrich C, Lobbrecht A, Spitz R, Mülhaupt R (1997) Acta Polymerica 48:41–46

Henglein A, Schnabel W, Wendenburg J (1969) Einführung in die Strahlenchemie. Verlag Chemie

Martakis N, Niaounakis M, Pissimissis D (1994) Gamma-sterilization effects and influence of the molecular weight distribution on the postirradiation resistance of polypropylene for medical devices. J Appl Polym Sci 51:313–328

Nojiri A, Sawasaki T (1985) Radiation crosslinking of polypropylene. Radiat Phys Chem 26:339–346

Pakula T, Geyler S, Edling T, Boese D (1996) Relaxation and viscoelastic properties of complex polymer systems. Rheol Acta 35:631–644

Rätzsch M (1999) Reaction mechanism to long-chain branched PP. J Macromol Sci A36:1759–1769

Sarcinelli L, Valenza A, Spadaro G (1997) Inverse response of polypropylene to gamma radiation under vacuum. Polymer 38:2307–2313

Sawasaki T, Nojiri A (1988) Radiation crosslinking of polypropylene. Radiat Phys Chem 31:877–886

Spadaro G, Valenza A (2000) Influence of the irradiation parameters on the molecular modifications of an isotactic polypropylene gamma-irradiated under vacuum. Polym Degrad Stabil 67:449–454

Spinks JWT, Woods RJ (1990) Introduction to radiation chemistry. Wiley, New York

Trinkle S, Friedrich C (2001) Van Gurp-Palmen-plot: a way to characterize polydispersity of linear polymers. Rheol Acta 40:322–328

Trinkle S, Walter P, Friedrich C (2002) Van Gurp-Palmen plot II – classification of long chain branched polymers by their topology. Rheol Acta 41:103–113

Waldron RW, McRae HF, Madison JD (1985) The effects of various monomers on crosslinking efficiency. Radiat Phys Chem 25:843–848

Yoshii F, Makuuchi K, Kikukawa S, Tanaka T, Saitoh J, Koyama K (1996) High-melt-strength polypropylene with electron beam irradiation in the presence of polyfunctional monomers. J Appl Polym Sci 60:617–623