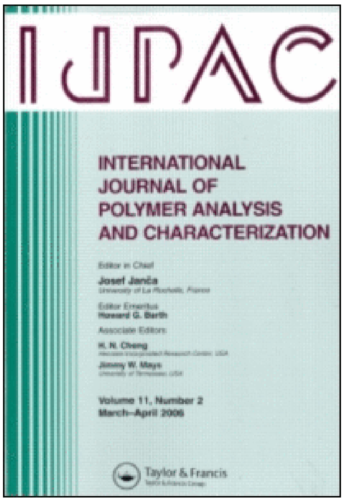

International Journal of Polymer Analysis and Characterization
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646643

Effect of Long-chain Branching and Microgels in the Viscoelastic Behavior of Ethylene—Propylene—Diene Copolymers

M. Demaio[a]; S. Caldari[a]; O. Chiantore[b]
[a] EniChem Research and Development Center, Ferrara, Italy [b] Department of Chemistry, IPM, University of Torino, Torino, Italy

To cite this Article Demaio, M. , Caldari, S. and Chiantore, O.(1999) 'Effect of Long-chain Branching and Microgels in the Viscoelastic Behavior of Ethylene—Propylene—Diene Copolymers', International Journal of Polymer Analysis and Characterization, 5: 1, 85 — 96

To link to this Article: DOI: 10.1080/10236669908014175

URL: http://dx.doi.org/10.1080/10236669908014175

Int. J. Polym. Anal. Charact.,
1999 Vol. 5, pp. 85–96
Reprints available directly from the publisher
Photocopying permitted by license only

Published by license under
the Gordon and Breach Science
Publishers imprint.
Printed in Malaysia.

Effect of Long-chain Branching and Microgels in the Viscoelastic Behavior of Ethylene–Propylene–Diene Copolymers*

M. DEMAIO[a], S. CALDARI[a] and O. CHIANTORE[b,†]

[a] *EniChem Research and Development Center, P.le Donegani 1, 44100 Ferrara, Italy;* [b] *Department of Chemistry IPM, University of Torino, Via Giuria 7, 10125 Torino, Italy*

(Received 6 March 1998; Revised 10 July 1998)

Ethylene–propylene–diene (EPDM) terpolymers with different amounts of microgel and long-chain branching have been characterized by dynamic mechanical experiments. Low frequency measurements were found particularly useful for revealing differences in viscoelastic properties of the samples. Loss factor values were of limited use, as they are influenced by sample molecular weights. Modified Cole–Cole plots were verified to be molecular weight independent, and could therefore be employed to detect molecular architecture variations. It was determined that long-chain branching and microgels are almost entirely localized in the higher molecular weight fractions of the investigated EPDM samples.

Keywords: EPDM; Elastomers; Viscoelastic properties; Rheology; Microgels; Long-chain branching

INTRODUCTION

Rheological measurements, and particularly dynamic mechanical experiments at different frequencies, have been often reported to be useful for investigating cross-linking reactions and for gel-point

---

* Presented in part at the 10th International Symposium on Polymer Analysis and Characterization (ISPAC-10), Toronto, Canada, August 1997.

[†] Corresponding author.

determination in polymer materials.[1–5] Basic differences arise from the fact that the storage modulus (G') of a polymer network is larger than the loss modulus (G'') at all frequencies; whereas in linear polymer chains, a cross-over between G' and G'' takes place at a given frequency.

It may be expected that the viscoelastic properties of polymers will be influenced not only by cross-linking and chain entanglements,[6] but also by the presence of topological constraints like slightly cross-linked polymer chains, or by architectural features like chain length distribution and long-chain branching (LCB).

In the case of polymer systems containing LCB or small amounts of slightly cross-linked material (microgel), the differences of rheological behavior, in comparison with linear molecules, may be fairly modest. However, their effects may be detected by performing measurements at low frequencies,[7] where long-range relaxation modes are more sensitive to molecular or morphological *defects*. Under such conditions, it is seen that dynamic viscosity values are larger, and loss factors lower, for the samples containing more LCB or microgel.

Another way to differentiate samples on the basis of differences in microgels and LCB is through log–log plots of loss moduli G'' as a function of storage moduli, G' in the so-called modified Cole–Cole plots.[8] Cole–Cole plots were originally formulated to represent time and frequency dependence of complex dielectric data,[9] and later adapted to the analysis of rheological behavior of polymers.[10] Logarithmic Cole–Cole plots give curves that are independent of polymer average molecular weights, and whose features can reveal differences of molecular architecture or morphology.[8]

In the production of ethylene–propylene–diene (EPDM) terpolymers, LCB may develop in the macromolecules depending on the diene content and on polymerization conditions.[11] LCB are likely to be concentrated in fractions or samples with larger molecular weights. With polymerization proceeding to high conversions, some cross-linked material may form, which will be present in the samples as a dispersed microgel. In order to control copolymer production process and product quality, the determination of LCB and microgels is of paramount importance.

In this paper we discuss the results obtained using rheological measurements for characterization of EPDM rubbers from the point of view of their LCB and microgel content.

EXPERIMENTAL

Materials

The samples investigated were two EPDM terpolymers (LG and HG) and the fractions obtained from both of them by selective extraction with solvent mixtures. The two EPDM samples were obtained by homogeneous Ziegler–Natta polymerizations with vanadium based catalysts. Irganox 1076 antioxidant (500–1000 ppm) was added to the samples. The selective extractions were performed by successively refluxing 6 g of polymer for 3–5 h in the proper solvent mixture and collecting the fraction separated at room temperature. No insolubles were found in the samples. Chemical compositions were determined with FT-IR and molecular weight characteristics measured by SEC. The data for whole samples and for the different fractions are reported in Table I and II, where the solvent mixtures employed in the fractionation are also indicated.

Characterization

SEC was performed on a Waters 150-C apparatus with a DRI detector (Waters Corp., Milford, MA) at 135°C in *o*-dichlorobenzene. Separations were obtained with four 30 cm × 0.78 PL gel, 10 μm columns (PL Laboratories, Shropshire, UK). Polymer solutions, 0.25% w/v concentrations, were prepared by heating the samples in the solvent at 150°C for 1 h. Average molecular weight values were calculated using the universal calibration approach.[12] Narrow distribution polystyrenes were

TABLE I Fractional solvent extraction of EPDM sample LG with different gel content

Fraction	*Solvent*	% wt	% *Propylene*	% *Ethylidene norbornene*	M_w	M_w/M_n
1	Ether/acetone 60/40	1.43	52.9	4.5	—	—
2	Ether/acetone 90/10	3.33	48.9	2.8	22,000	1.9
3	Ether/acetone 95/5	2.05	36.6	2.9	34,000	1.8
4	Ether	1.98	28.0	3.7	29,000	1.7
5	Ether/hexane 95/5	1.42	26.8	3.8	36,000	1.7
6	Ether/hexane 90/10	11.21	28.3	4.0	54,000	1.6
7	Ether/hexane 80/20	40.24	25.9	4.1	99,000	1.5
8	Hexane	38.34	25.4	4.2	200,000	1.7
Unfractionated			27.5	3.7	165,000	2.7

TABLE II Fractional solvent extraction of EPDM sample HG with different gel content

Fraction	*Solvent*	% wt	% *Propylene*	% *Ethylidene norbornene*	M_w	M_w/M_n
1	Ether/acetone 60/40	1.70	51.2	6.0	—	—
2	Ether/acetone 90/10	3.42	43.8	2.1	19,000	1.8
3	Ether/acetone 95/5	3.76	34.6	3.4	31,000	1.7
4	Ether	4.88	30.2	4.0	39,000	1.8
5	Ether/hexane 95/5	4.78	27.7	4.1	49,000	1.5
6	Ether/hexane 90/10	6.44	27.2	4.3	70,000	1.5
7	Ether/hexane 80/20	34.86	26.2	4.6	53,000	2.3
8	Hexane	40.16	24.2	4.7	252,000	1.8
Unfractionated			27.2	4.2	177,000	2.9

used as primary standards, and Mark–Houwink coefficients for the EPDMs were calculated from those of linear polyethylene and of polypropylene taking into account sample compositions according to the method of Scholte.[13]

Chemical composition of samples and fractions were determined by FTIR, on a Perkin-Elmer (Norwalk, CT) 1750 instrument. The absorption bands at 1379 and 1464 cm^{-1} were used for propylene and ethylene content respectively, whereas ENB was determined from measurement of the absorbance of peak at 1685 cm^{-1}.[14,15] Standard polymers enriched with carbon-14 and analyzed with radiochemical techniques were used to calibrate the FT-IR method.

Viscoelastic measurements were obtained with a Rheometrics RDA II dynamic mechanical analyzer (Rheometrics Inc., Piscataway, NJ), parallel plate geometry, on 25-mm diameter polymer disks. Measurements were also done with a Polymer Laboratories DMTA MKII (Shropshire, UK) on 12-mm and 7-mm diameter disks. Frequency sweeps were carried out at 130°C. Frequencies are expressed in Hz, for data obtained on Rheometrics apparatus, and in rad/s for the DMTA system (1 rad/s = 0.16 Hz).

RESULTS AND DISCUSSION

The two EPDM samples investigated in this work had similar characteristics in terms of average chemical composition, apparent molecular

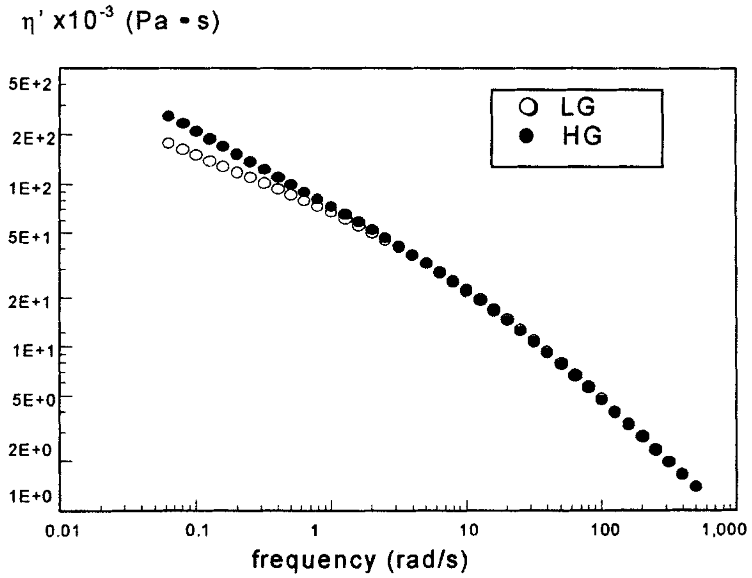

FIGURE 1 Dynamic viscosity values, at 130°C and different frequencies, of the two unfractionated EPDM samples with different gel content.

weight averages and distributions (Table I). They showed differences, however, as far as their rheological properties are concerned.

The results of dynamic viscosity measurements at 130°C for the two samples, in the frequency range 10^{-1}–10^{-3} rad/s, are reported in Figure 1. At frequencies lower than 1 rad/s the viscosity of sample HG is larger, and the difference increases with decreasing frequency measurement.

Cross-linking and LCB tend to increase zero-shear viscosity and storage modulus of polymers.[6] The low frequency behavior of the two EPDM samples may be therefore attributed to a different amount of LCB and cross-linked particles present in the two samples, which will have a particular effect on the slow chain relaxation modes.

Another way of looking at the differences of the rheological behavior between the two EPDM samples is through the plot of loss factor values, $\tan\delta = G''/G'$, at the different frequencies, in Figure 2. The differences are more easily appreciated, as the loss factor decrease for the EPDM with higher gel content is already clearly visible at *ca.* 10 rad/s.

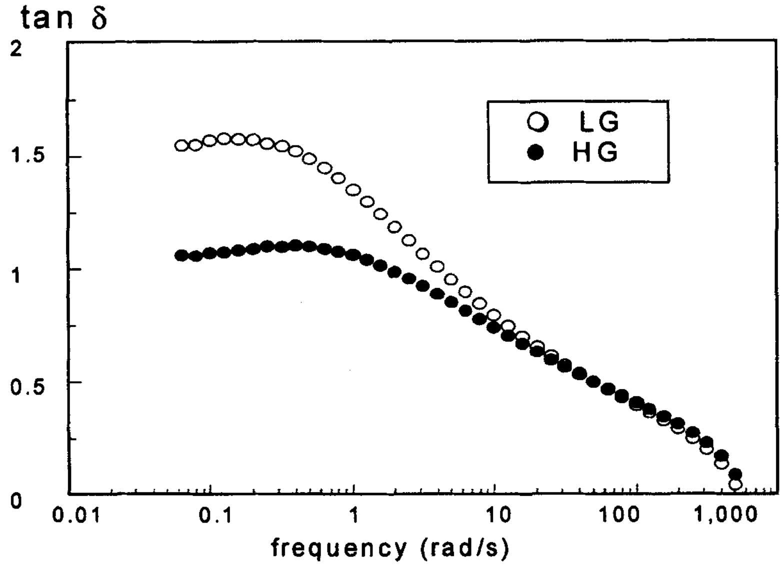

FIGURE 2 Loss factor values, tan δ, of the two unfractionated EPDM samples at 130°C and different frequencies.

The same data, plotted as modified Cole–Cole plots, $\log G''$ vs $\log G'$ at each frequency, are shown in Figure 3. In the low frequency region, G' values of the HG sample are always larger than in the other sample for the same G''.

Cole–Cole plots have been shown to be affected by features of sample morphology, and particularly by the presence of crystalline structures.[8] The presence of such an effect may be revealed by comparing G'' vs G' curves measured at different temperatures: a single curve is obtained when all crystalline structures have been eliminated by melting.

With the EPDM samples investigated, contributions from crystalline regions to the Cole–Cole plot displacements were completely absent at 130°C. This was verified by performing the same measurements at 160°C. As seen from the results in Figure 4, the points at the two different temperatures lie on a common curve for each sample.

A more detailed structural analysis was carried out on the fractions obtained from the two EPDM samples by selective solvent extraction. Eight fractions were obtained from the soluble part of each sample.

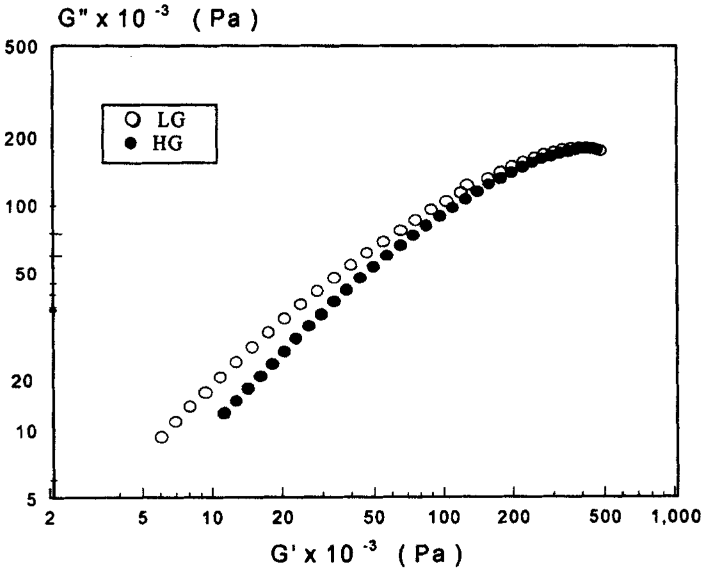

FIGURE 3 Modified Cole-Cole plots for the two unfractionated EPDM samples at 130°C.

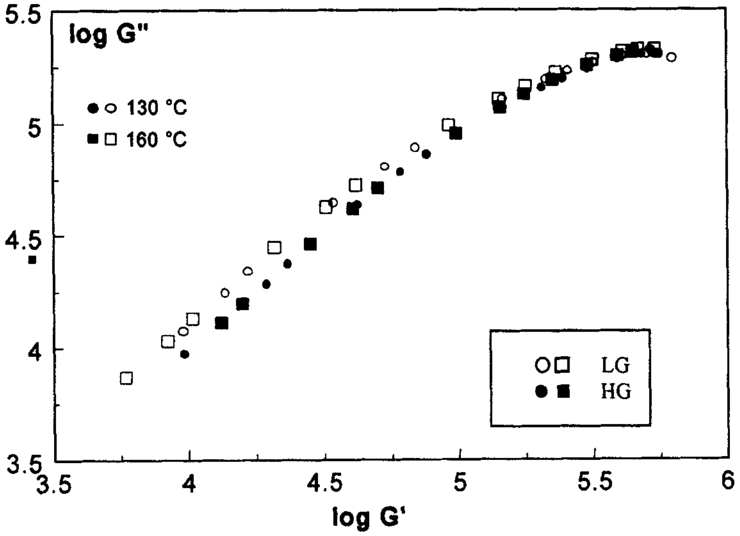

FIGURE 4 Modified Cole-Cole plots at 130° and 160°C for the two unfractionated EPDM samples with different gel content.

The fractions were characterized in terms of chemical compositions and molecular weights, and the results are reported in Table I and II. The fractions from the two samples had different average molecular weights, but revealed very similar chemical compositions, with the exception of the two lower molecular weight fractions, which represent in each case only 6–9% of the total polymer.

The dynamic mechanical behavior of the fractions was measured in the whole accessible frequency range. The tan δ curves are obviously strongly influenced by the average molecular weights of the fractions. An example is shown in Figure 5, where data relative to fractions 7 and 8 of HG sample are reported. Weight-average molecular weights of the fractions are 53,000 and 252,000, respectively. The maximum of tan δ, corresponding to the disentanglement peak, is shifted to lower frequency with increasing molecular weights, due to slower chain relaxations. The shape of the two curves is, however, very similar, and in fact they can be superimposed quite well by just performing a manual shift, as seen in Figure 6 where the curve passing through the points of fraction 7 was moved to lower frequencies. The result is a

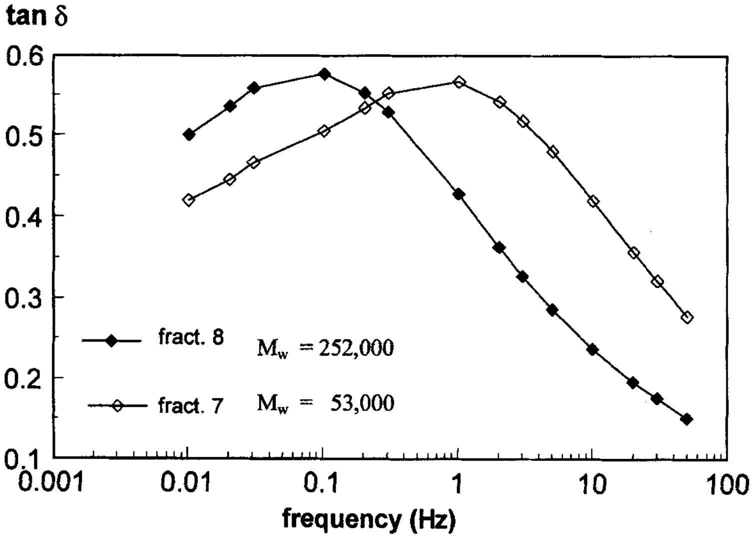

FIGURE 5 Tan δ values determined at different frequencies and 130°C for fractions 7 and 8 of EPDM sample HG.

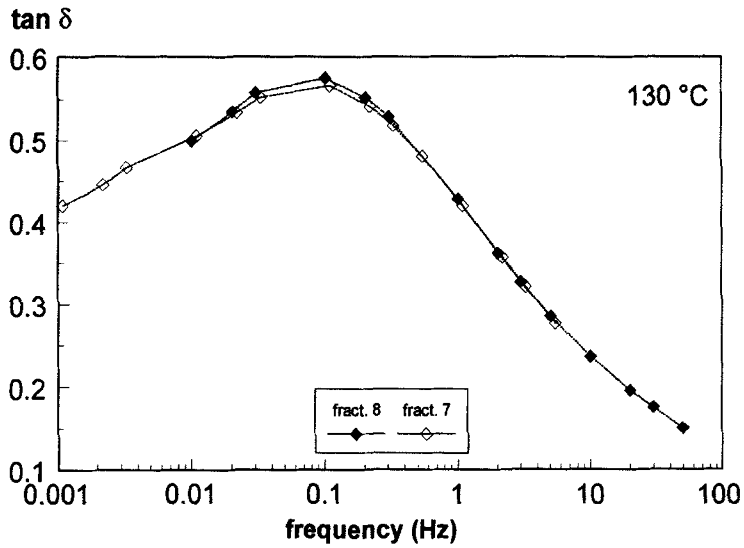

FIGURE 6 Master curve obtained by application of a constant shift factor to tan δ values of fraction 8.

master curve for fraction 8, with tan δ values extended to lower frequencies.

In samples with the same structure, morphology and architecture, it may be expected that rheological measurements will reveal chain relaxations at frequencies increasing with decreasing molecular weights. The superposition data in Figure 6 demonstrates that there are no differences between the two fractions, other than in molecular weight.

Confirmation of such finding comes from Figure 7, where the data relative to the same two fractions 7 and 8 are plotted as $\log G''$ vs $\log G'$. A common curve is obtained, in agreement with the fact that Cole–Cole plots are molecular weight independent,[8] demonstrating that no other structural difference exists between the two fractions. The Cole–Cole plots were therefore employed for investigating the rheological differences between the fractions of the two different EPDM samples.

Figure 8 shows the comparison of results for the whole polymer samples, and for fractions 6, 7 and 8, having the highest molecular weights. The amount of polymer in the other fractions, with lower

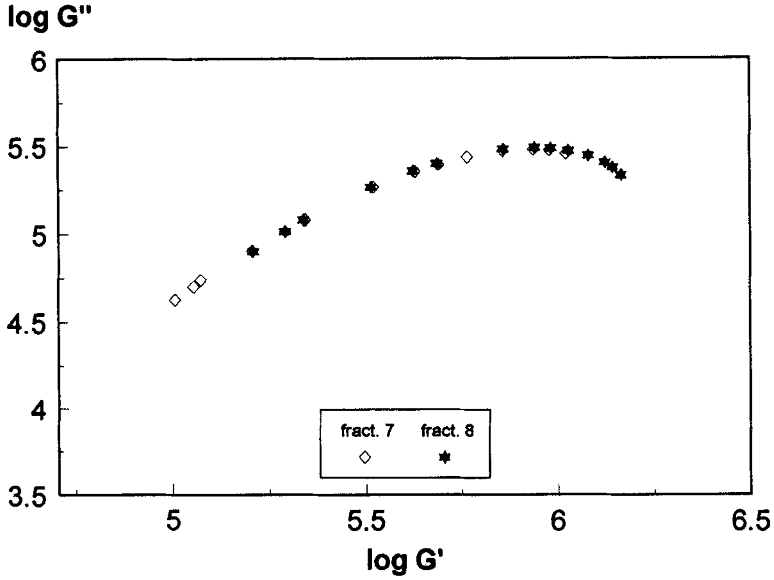

FIGURE 7 Common Cole–Cole plot for fractions 7 and 8 of HG sample.

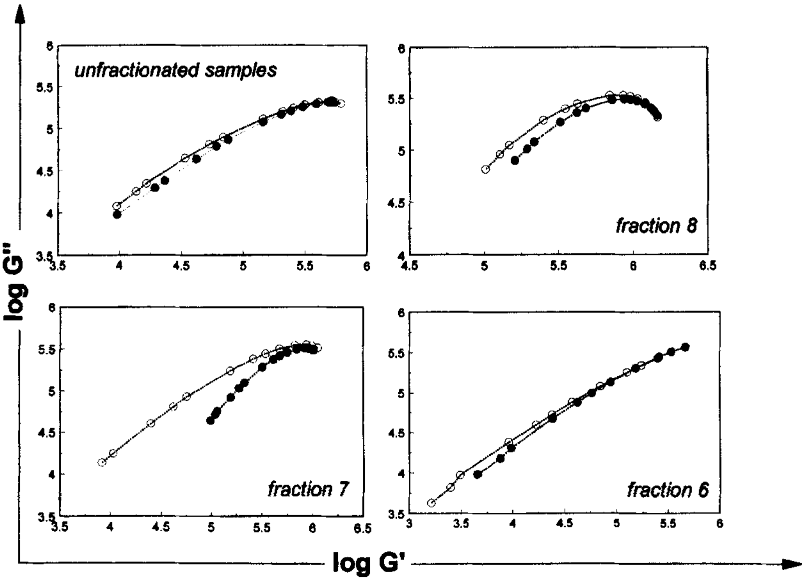

FIGURE 8 Comparison of Cole–Cole plots for LG (○) and HG (●) EPDM: unfractionated samples, and highest molecular weight fractions.

molecular weights, was not enough for the viscoelastic measurements. The G' displacement to higher values, found in the whole HG sample, is also present in the measured fractions due to a larger amount of LCB or cross-linked particles in this sample. The effect is particularly relevant in fractions 7 and 8, in agreement with the expectancy that LCB and microgels are mostly concentrated in the higher molecular weight chains of a polymer.[16] It is also worth noting that fractions 7 and 8 account for *ca.* 75% of the total polymer.

CONCLUSIONS

The results reported here for EPDM terpolymers with different, low amounts of gel confirm the validity of dynamic mechanical experiments at low frequencies for revealing the presence of topological constraints, microgels or LCB, in polymer samples. Cross-linked material in EPDM may have been derived from unwanted reactions of the diene moiety, with the initial production of branched structures. It is therefore reasonable to assume that the sample with higher gel content will also contain more LCB in the soluble portion.

The $\tan\delta$ values measured at low frequencies were found to be very sensitive probes for revealing differences in viscoelastic properties of the EPDMs. However, since these values are strongly influenced by molecular weights, their use is of limited value. It has been verified, however, that modified Cole–Cole plots are molecular weight independent, and can be employed to detect molecular architecture variations. The effect brought by the restrictions to molecular mobility is a displacement of low frequency data towards higher G' values at constant values of G''.

In the EPDM sample here investigated LCB and microgels were found to be almost entirely localized in the fractions with higher molecular weights.

References

[1] Chambon, F., Petrovic, Z.S., MacKnight, W. and Winter, H.H. (1986) *Macromolecules*, **19**, 2146.
[2] Winter, H.H., Morganelli, P. and Chambon, F. (1988) *Macromolecules*, **21**, 532.
[3] Scanlan, J.C. and Winter, H.H. (1991) *Macromolecules*, **24**, 47.

[4] Schwittay, C., Mours, M. and Winter, H.H. (1995) *Faraday Discuss*, **101**, 93.
[5] Raghavan, S.R., Chen, L.A., McDowell, C., Khan, S.A., Hwang, R. and White, S. (1996) *Polymer*, **37**, 5869.
[6] Ferry, J.D. (1980) *Viscoelastic Properties of Polymers*, Wiley, New York.
[7] Scholtens, B.J.R. and Welzen, T.L. (1981) *Makromol. Chem.*, **182**, 269.
[8] Harrel, E.R. and Nakajima, N. (1984) *J. Appl. Polym. Sci.*, **29**, 995.
[9] Cole, K.S. and Cole, R.H. (1941) *J. Chem. Phys.*, **9**, 341.
[10] Graessley, W.W. and Roovers, R. (1979) *Macromolecules*, **12**, 959.
[11] Ver Strate, G. (1986) *Ethylene–propylene-elastomers* In *Encyclopedia of Polymer Science and Engineering* (Wiley, New York), Vol. 6, p. 522.
[12] Benoit, H., Grubisic, Z., Rempp, P., Decker, D. and Zilliox, J.G. (1966) *J. Chem. Phys.*, **63**, 1507.
[13] Scholte, Th.G., Meijerink, N.L.J., Schoffelers, H.M. and Brands, A.M.G. (1984) *J. Appl. Polym. Sci.*, **29**, 3763.
[14] Tosi, C. and Simonazzi, T. (1973) *Angew. Makromol. Chem.*, **32**, 153.
[15] Gardner, I.J. and Ver Strate, G. (1973) *Rubber Chem. & Technol.*, **46**, 1019.
[16] Kuhne, J.K. and Kautt, K. (1984) *Kauts Gummi Kunststoffe*, **37**, 101.