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ORIGINAL CONTRIBUTION

R. Schinner
T. Wolff

Defined photo-cross-linking and viscometric data II. Photo-cross-linking versus coordinative cross-linking

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R. Schinner · T. Wolff (✉)
Technische Universität Dresden,
Institut für Physikalische Chemie und
Elektrochemie, 01062 Dresden, Germany

Abstract Cross-linking in solution of polystyrene containing phenylindene units has been brought about via photochemical dimerization in chloroform or via iron complexation of the indene groups in tetrahydrofuran [bis(indenyl)iron formation]. Both irradiation and complexation lead to enhanced viscosity and eventual non-Newtonian flow of the solutions, indicating the formation of cross-links, which were proven by absorption spectroscopy. Depending on concentration, molecular weight and phenylindene content, distinctions in the two methods arose, such as enhanced intramolecular cross-linking in the photochemical case as revealed by flow behavior and zero-shear viscosities. Cyclovoltammetric investigations of the iron-complexed polymers show inhibition of iron oxidation due to the presence of the surrounding polymer.

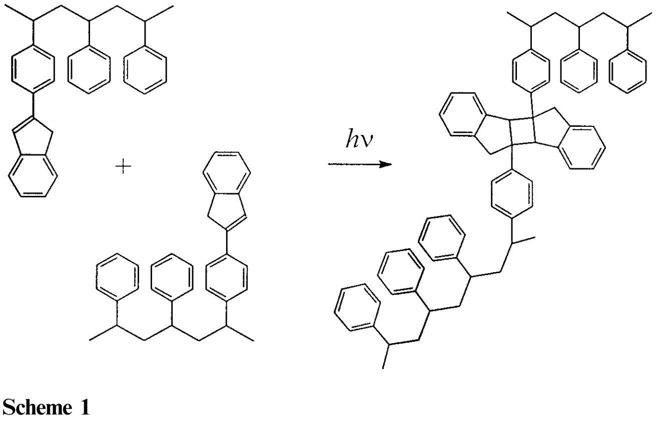
Key words Polystyrene solution · Cross-linking · Viscometry · Bis(indenyl)iron

Introduction

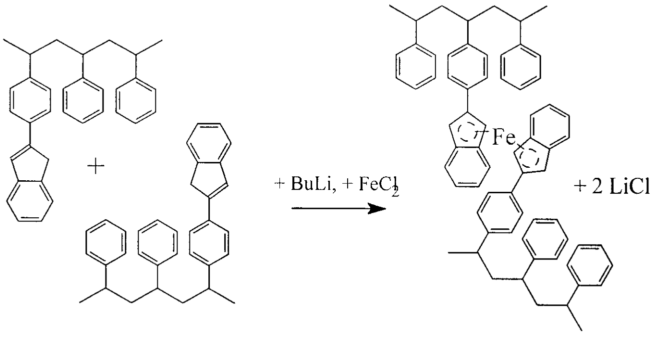
While cross-linking via photochemical dimerizations is widely employed to produce cross-links in polymers [1–4] (but less often in polymer solutions [5, 6]), the use of metal complexation to realize cross-links is less common [7], although various linear coordination polymers [8–10] and metallomesogenic polymers [11] have been described. In an earlier article [5] we reported rheological investigations in solutions of poly(styrene-*co*-(4-styryl)indene), which is capable of forming cross-links via photodimerization of the phenylindene moieties (Scheme 1).

Since – analogous to the known formation of stable 2:1 complexes of cyclopentadienyl anions and iron(II) (ferrocene) – the reaction of indenyl anions and Fe^{2+} cations leads to neutral bis(indenyl)iron [12–18], we expected this reaction to be suitable to form cross-links in solutions of poly(styrene-*co*-(4-styryl)indene) (Scheme 2).

Here we present UV spectroscopic and rheological investigations aimed at comparing these two methods of cross-linking. While ferrocene is known to be stable against oxidation as revealed by perfectly reversible cyclic voltammograms (Fig. 1), bis(indenyl)iron is reported to be less stable [17]. In order to test the stability of our complexed copolymers we therefore carried out additionally a cyclovoltammetric study.



Scheme 1



Scheme 2

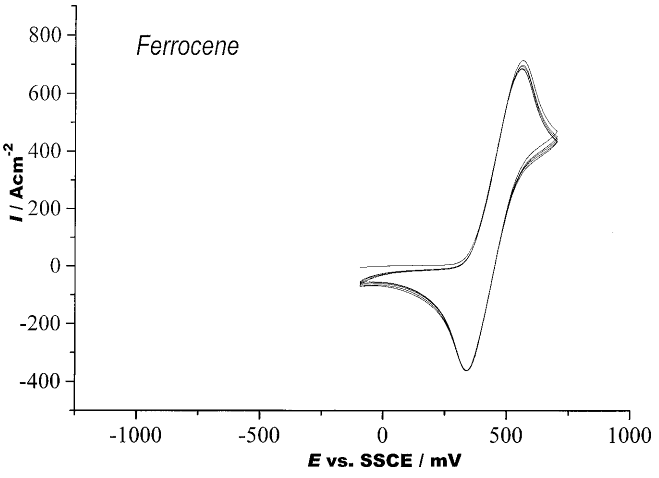


Fig. 1 Cyclic voltammogram of ferrocene

Experimental

Preparation of poly(styrene-*co*-(4-styryl)indene) and bis(indenyl)iron

The preparation of sample N1 of poly(styrene-*co*-(4-styryl)indene) was performed as follows. Styrene (10.4 g) and (4-styryl)indene (1.05 g) were dissolved in 25 ml toluene. The copolymerization was started at 80 °C by the addition of 0.02 g azobis(isobutyronitrile) (AIBN). The mixture was kept at 80 °C for 3 h; after 1.5 h a second portion of AIBN (0.02 g) was added. The weight-average molecular weight (M_w) and the molecular-weight distribution (M_w/M_n) determined via gel permeation chromatography (GPC) analysis were 3.0×10^{-4} g/mol and 2.9, respectively. The indene content of the polymer was 5.9% according to NMR analysis. Samples N2–N4 were prepared analogously. N2: indene content 1.9 mol%, M not determined; N3: indene content 4.3 mol%, $M_w = 7.8 \times 10^4$ g/mol, $M_w/M_n = 4.9$; N4: indene content 6.5 mol%, $M_w = 9.3 \times 10^4$ g/mol, $M_w/M_n = 3.6$. Compared to the copolymerization in aqueous micellar solution described previously [5] the molecular weights achieved here were lower.

Bis(indenyl)iron was prepared as described in Ref. [17].

Apparatus

For rheological experiments a rotating viscometer (Suck V10) was employed using Mooney–Eward geometry in Couette mode. All rheological experiments were performed in chloroform as solvent at (20 ± 0.5) °C. UV–vis spectra were recorded using a home-made UV spectrometer using a photodiode charge-coupled-device detector from Alton Instruments (Lambda Series LS-2000) which was calibrated for wavelengths from 225 to 843 nm. Samples prepared at equal concentrations for irradiation and rheological experiments, respectively, were diluted for UV measurements by a factor of 127.5. For GPC analysis a JASCO apparatus, Waters ultrastyragel columns and a Wyatt Technology Dawn DSP multiangle light scattering detector were employed.

Irradiations

Stirred chloroform solutions under an argon atmosphere (the concentrations are given in Table 1) were irradiated through the

Table 1 Ratios of the change in zero-shear viscosity, $\Delta\eta_0$, and in UV absorption, ΔA, (obtained upon cross-linking) for four solutions of the copolymer in chloroform, differing in molecular weight, M, polydispersity M_w/M_n, (ratio of weight-average and number-average molecular weight), mole fraction of chromophore, y_C, weight fraction of polymer in solution, g_P, and degree of cross-linking induced either by addition of varying weight fractions, g, of FeCl$_2$ (with respect to copolymer) or by irradiation for various times, t_{irr}

Copolymer	$M/10^4$ (gmol^{-1})	M_w/M_n	$100y_C$ (%)	$100g_P$ (%)	$100g$(FeCl$_2$) (%)	t_{irr} (min)	$10^{-5}(\Delta\eta_0/\Delta A)$ (Pas)
N1	3.0	2.9	5.9	20.0	15.8	–	2.5
N1	3.0	2.9	5.9	20.0	30	–	3.3
N1	3.0	2.9	5.9	20.0	–	1	0.07
N1	3.0	2.9	5.9	20.0	–	4	0.11
N2	7.8	4.9	1.9	17.0	10	–	0.6
N2	7.8	4.9	1.9	17.0	30	–	33.5
N3			4.3	26.0	10	–	1.1
N3			4.3	26.0	–	1	10.7
N3			4.3	26.0	–	3	331
N4	9.3	3.6	6.5	11.0	8	–	0.08
N4	9.3	3.6	6.5	11.0	16	–	1,500
N4	9.3	3.6	6.5	11.0	–	0.75	1.07
N4	9.3	3.6	6.5	11.0	–	1	33
N4	9.3	3.6	6.5	11.0	–	2	43

gas–liquid interface by employing Pyrex-filtered light of a 100-W mercury lamp (AMKO). A low quantum flux must be ensured to allow sufficient stirring to avoid network-film formation at the irradiated interface.

Iron complexation of poly(styrene-*co*-(4-styryl)indene)

A stirred solution of 1.0 g poly(styrene-*co*-(4-styryl)indene) (sample N1, Table 1) in 10 g tetrahydrofuran (THF) was cooled to −70 °C. *N*-Butyllithium (1 ml, 2.5 M in hexane, i.e., 2.5 mmol) was added dropwise. Then the mixture was warmed to 40 °C and a solution of 1.58 mg $FeCl_2$ in 10 g THF (half the molar amount of lithium) was added dropwise. Then the solvent was evaporated. The product was freed of salt by dissolving the cross-linked polymer twice in toluene and precipitating it by addition of ethanol. The product was dried in vacuo (and dissolved in chloroform for UV and viscometric measurements). Samples N2–N4 (Table 1) were treated analogously.

Viscometry

The zero-shear viscosities, η_0, shown in Table 1 were derived from the initial slopes of the flow curves in chloroform. To obtain the flow curves the shear rate, $d\gamma/dt$, was increased linearly from 0 to 100 s^{-1} within 50 s, kept at 100 s^{-1} for 10 s, and decreased linearly from 100 to 0 s^{-1} within 50 s. A slower increase of $d\gamma/dt$ in the time ramp did not affect the zero-shear viscosity values. Stress relaxation curves were recorded after preshearing for 12 s at shear rates of 30, 51 and 90 s^{-1}.

Intrinsic viscosities and overlap concentrations, c^*, were determined at $d\gamma/dt = 50\ s^{-1}$ in chloroform. Sample N4 (Table 1, nonirradiated and irradiated for 0.75 min) was multiply diluted and the reduced viscosities measured ($\eta_{red} = \eta_{sp}/c$, where c is the mass concentration) were plotted against c. The intersection of the two lines joining the points at higher and at lower concentrations was taken as the overlap concentration, c^*.

Cyclic voltammetry

Experiments were performed in CH_2Cl_2 as a solvent (0.05 g substance per 10 cm^3 solvent) using an EG&G Princeton Applied Research (model 263A) apparatus (scan rate: 50 mV/s; electrodes: platinum; electrolyte: 0.25 M tetrabutylammonium perchlorate).

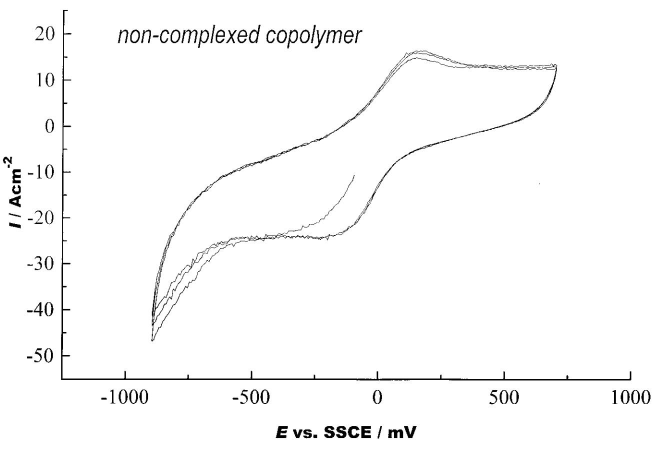


Fig. 2 Cyclic voltammogram of poly(styrene-*co*-(4-styryl)indene)

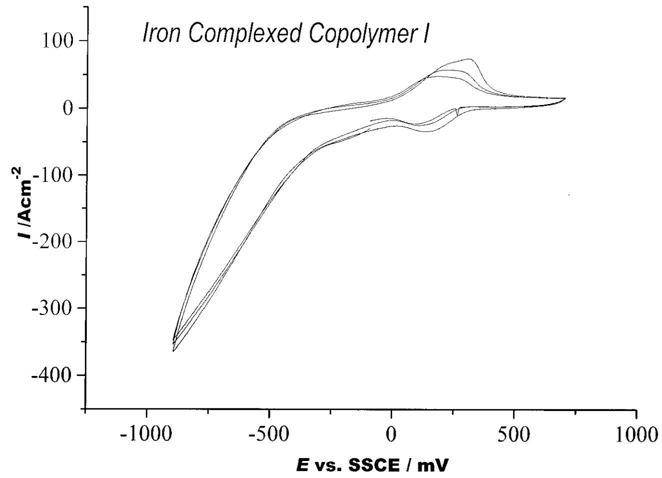


Fig. 3 Cyclic voltammogram of poly(styrene-*co*-(4-styryl)indene) cross-linked via bis(indenyl)iron formation (low iron content)

Results

Characterization of bis(indenyl)iron cross-linked poly(styrene-*co*-(4-styryl)indene)

Cyclic voltammograms (plots of current versus potential) of ferrocene, noncomplexed poly(styrene-*co*-(4-styryl)indene) and complexed poly(styrene-*co*-(4-styryl)indene) are reproduced in Figs. 1, 2, 3 and 4. In agreement with literature data [19], the cyclic voltammogram of ferrocene (Fig. 1) exhibits an oxidation peak of Fe^{2+} at 550 mV and a reduction peak of Fe^{3+} at 350 mV (versus standard calomel electrode). The reproducibility of oxidation and reduction (as revealed by repeating the runs four times) indicates the reversibility of the redox process. In bis(indenyl)iron we did not find

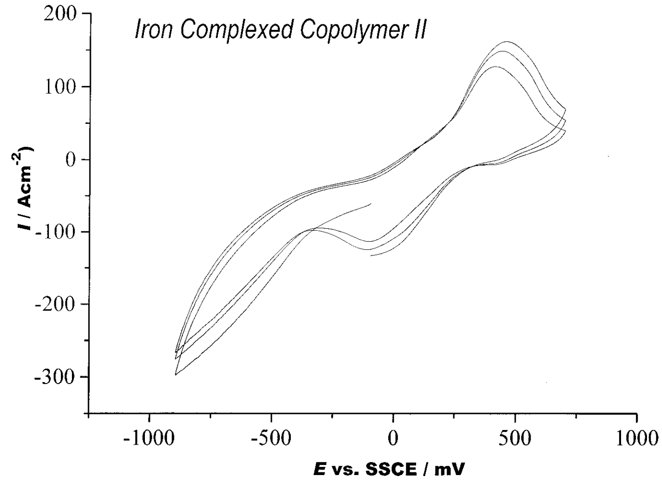


Fig. 4 Cyclic voltammogram of poly(styrene-*co*-(4-styryl)indene) cross-linked via bis(indenyl)iron formation (high iron content)

features matching those in ferrocene: badly reproducible cyclic voltammograms were obtained at reduced current.

The cyclic voltammograms of the polymers differ. While non-cross-linked poly(styrene-*co*-(4-styryl)indene) (Fig. 2) exhibits oxidation and reduction peaks at 150 and −160 mV, respectively, at very low current, the complexed polymer with low iron content (Fig. 3) shows an increase in the current and, in addition to the polymer features, redox peaks similar to bis(indenyl)iron appear, which are attributable to the Fe^{2+}/Fe^{3+} redox pair. The redox peaks diminish with the number of cycles. In the complexed polymer with higher iron content (Fig. 4), however, we observe a strong increase in the current (compared to the pure copolymer) and an oxidation potential shifted in the direction of the ferrocene or bis(indenyl)iron sample. The cyclic voltammogram changes with the number of cycles, indicating irreversible processes. This effect, however, is less pronounced than in the bis(indenyl)iron system without copolymer. In mixtures of the copolymer and free ferrocene or bis(indenyl)iron very similar cyclic voltammograms were obtained, showing Fe^{2+}/Fe^{3+} peaks decreasing with the number of cycles.

Choice of solvent for rheological experiments

Unfortunately the irradiation and the iron complexation cannot be performed in the same solvent. Owing to the chemistry of lithium the latter is not possible in chloroform (the solvent mostly used in irradiations), whereas irradiation in THF (suitable for iron complexation) leads to poor irradiation results as reported previously [5]. Therefore, photochemical cross-linking was performed in chloroform but iron complexation was performed in THF, and the isolated complexation product was dissolved in chloroform for use in both the UV spectroscopic and the rheological comparison of photochemical and bis(indenyl)iron cross-linking. In this way we exclude possible different polymer structures existing in the two solvents that might affect the rheology of the systems. When the bis(indenyl)iron cross-linked polymer was kept under argon during the preparation until shortly before the viscometric measurements, subsequent UV analysis did not show changes in comparison to the starting material that can be attributed to oxidation of the iron complex.

Typical experimental data are reproduced in Figs. 5 and 6 comparing changes in the absorption spectra and in the corresponding flow curves of a chloroform solution of copolymer N4 upon photochemical cross-linking, and upon bis(indenyl)iron cross-linking. In Table 1 the rheological and UV spectroscopic data are summarized for samples N1–N4. The ratios of the changes of zero-shear viscosity (initial slopes of flow curves) and of absorption vary largely and may be taken as a measure for the efficiency of cross-linking. Inspection of the data clearly reveals that these ratios are larger in the bis(indenyl)iron cross-linked materials compared to the photochemically cross-linked samples. Since the flow curves are reproducible (after 30 min of rest), significant breaking of the coordinative cross-links upon shearing does not take place.

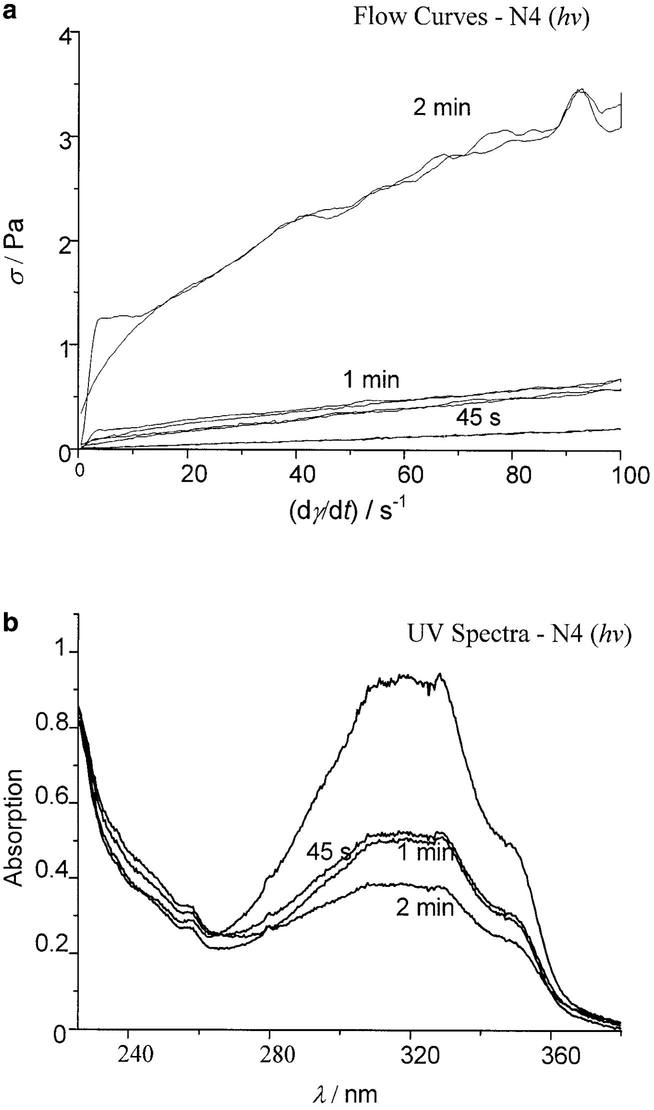


Fig. 5 **a** Flow curves (shear stress versus shear rate) and **b** absorption changes (phenylindene chromophore) for sample N4 (Table 1) at various degrees of photochemical cross-linking (irradiation times)

An example of further rheological investigation is shown in Fig. 7 for sample N2, which becomes viscoelastic upon cross-linking by bis(indenyl)iron. The figure displays relaxation spectra [distribution of stress relaxation time constants, $H(\tau)$] which were obtained from stress relaxation curves using the equation

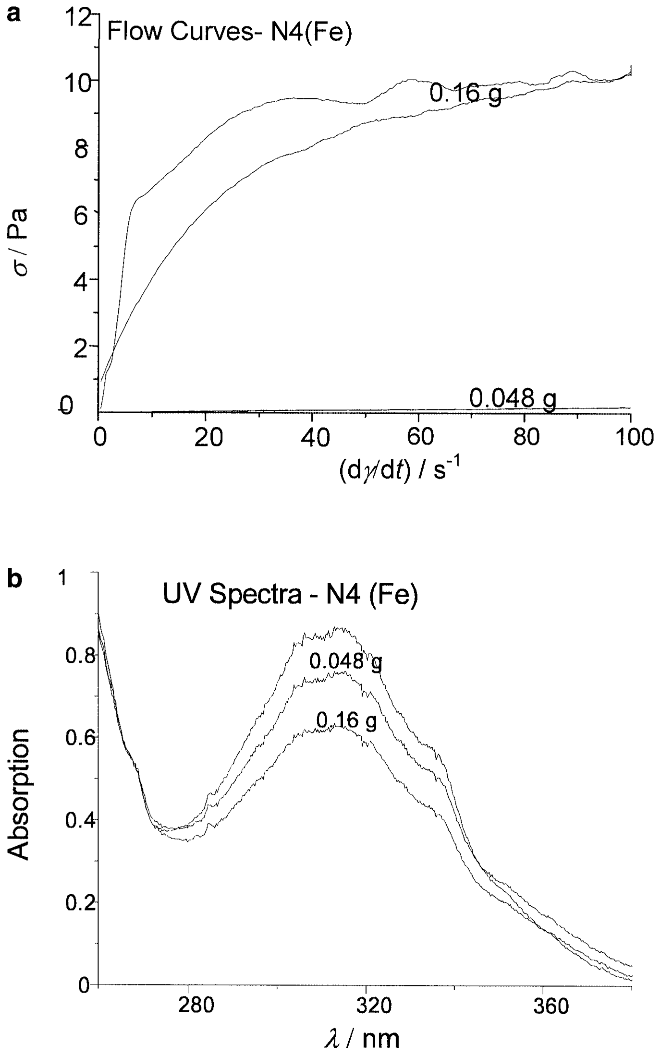


Fig. 6 **a** Flow curves (shear stress versus shear rate) and **b** absorption changes for sample N4 (Table 1) at various degrees of bis(indenyl)iron cross-linking (addition of $FeCl_2$)

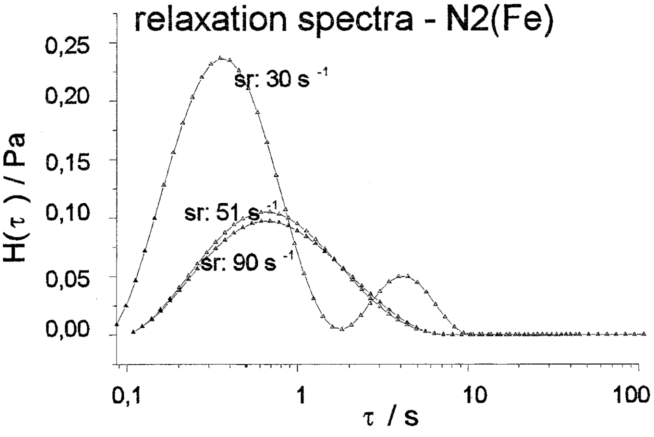


Fig. 7 Distribution, H, of stress relaxation time constants, τ, in a viscoelastic solution of sample N2 (Table 1) after bis(indenyl)iron cross-linking

$$\sigma(t) = \int_0^\infty H(\tau)\exp(-t/\tau)\mathrm{d}\ln\tau \ , \tag{1}$$

where σ denotes the shear stress, t the time and τ the time constant of the relaxation process. To calculate $H(\tau)$ using Eq. (1) we employed the evaluation procedure described previously [20, 21], i.e., Provencher's CONTIN program was applied [22, 23] (originally developed for the evaluation of light scattering data). It was possible to fit the stress relaxation curves exponentially using reciprocal τ values of the maxima in the H versus τ diagrams as decay constants. The two maxima observed after preshearing at a low shear rate, $\mathrm{d}\gamma/\mathrm{d}t = 30\ \mathrm{s}^{-1}$, indicate that two stress relaxation processes occur. At higher shear rates (51 and 90 s^{-1}), however, only a single relaxation process with an intermediate time constant is revealed. In order to test the consistency of the data evaluation (ill posed problem in Eq. 1) we checked that the stress relaxation curves could be fitted satisfactorily using the reciprocal τ values of the maxima in the $H(\tau)$ curves as decay constants.

For sample N4 an intrinsic viscosity of 0.09 $\mathrm{cm^3g^{-1}}$ was found, which changed to 0.37 $\mathrm{cm^3g^{-1}}$ after 0.75 min irradiation. From plots of the reduced viscosities, η_{red}, versus mass concentration, c, the corresponding values of c^* were obtained to be 28 and 47 $\mathrm{gdm^{-3}}$, respectively. In the bis(indenyl)iron complexed samples the determination of c^* failed, probably owing to gel formation.

Discussion

Cyclic voltammograms

The observed features may be interpreted in the following way:

1. Ferrocene versus bis(indenyl)iron: the irreproducibility of the cyclic voltammograms of bis(indenyl)iron was expected, since the stability of bis(indenyl)iron against oxidation in solution is less than that of ferrocene [16]; however, the oxidation process with various oxidants does not result in the formation of bis(indenyl)iron(III) [17].
2. In the ferro(bisindenyl) cross-linked polymers the cyclic voltammograms clearly show irreversible features. These can again be understood when the previously reported fact is considered that bis(indenyl)iron [containing iron(II)] does not form bis(indenyl)iron(III) compounds [17]. The comparatively low currents decreasing with the number of cycles indicate polystyrene moieties covering the electrode, thus preventing the bis(indenyl)iron moieties from reacting. Coverage of the electrodes by the copolymer also

explains the decreasing of the ferrocene peaks in mixtures of copolymer and ferrocene.

Viscometry

UV analysis does not reveal changes in the bis(indenyl)iron cross-linked copolymer for cases in which it was kept under argon during the preparation (until shortly before the viscometric measurements). At a similar number of cross-links (as revealed by the absorption change), the increase in viscosity observed after bis(indenyl)iron formation exceeds that observed after photochemical cross-linking (Table 1). Moreover, the irradiated samples exhibit Newtonian flow up to the consumption of half of the chromophores (cf. Figs. 5, 6) in contrast to bis(indenyl)iron cross-linking (Figs. 7, 8). Both these features indicate that more intra(macro)molecular cross-linking takes place during the photochemical procedure. This effect may be related to the fact that irradiation light can penetrate only a few micrometers inside the solution, taking into account that absorption coefficients of the chromophore are about 10^4 dm^{3}mol^{-1}cm^{-1}. If we further consider that the photodimerization of two phenylindene moieties can take place only within the lifetime of an excited phenylindene (less than 2 ns [24]), intramolecular dimerization is more likely in spite of stirring. Another possible origin of the different cross-linking mechanisms may arise from distinctions in the polymer solution structure at the beginning of cross-linking owing to the different solvents and temperatures.

Two relaxation processes in sheared viscoelastic solutions of bis(indenyl)iron cross-linked N2 can be distinguished after preshearing at 30 s^{-1} (Fig. 7). If we exclude chain scission in these systems at low shear rates, in principle three relaxation processes may be considered: relaxation of network segments, movement of non-cross-linked chains or chain ends along their contour lengths, and sliding of entanglements [25]. Without a valid theoretical model of the system we cannot decide which two of the three possible processes are active and why they merge at higher shear rates; however, the relaxation behavior appears less complicated than in photochemically cross-linked viscoelastic samples [5], which exhibit up to three relaxation processes. This again indicates different network formation mechanisms for each of the two methods, leading to a more regular network in the bis(indenyl)iron case.

Conclusion

Cross-linking of poly(styrene-*co*-(4-styryl)indene) via bis(indenyl)iron formation is possible in THF solution. Accordingly, flow curves of solutions of the cross-linked material reveal increased viscosity compared to the non-cross-linked polymer. Depending on the concentrations and the degree of cross-linking, non-Newtonian flow occurs. Compared to photochemical cross-linking more intermolecular links are formed, i.e., more homogeneous networks (gels) can be obtained.

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