Styrene–Isoprene Block Copolymers.
II. Hydrogenation and Solution Properties

R. VELICHKOVA,[1,*] V. TONCHEVA,[1] C. ANTONOV,[1,†] V. ALEXANDROV,[1,†] S. PAVLOVA,[2] L. DUBROVINA,[2] and E. GLADKOVA[2]

[1]Central Laboratory for Polymers, Bulgarian Academy of Sciences, 1040 Sofia, Bulgaria and [2]Institute of Elementoorganic Compounds, USSR Academy of Sciences, Moscow, USSR

SYNOPSIS

Styrene–isoprene block copolymers with a different degree of monomer distribution are hydrogenated with homogeneous catalysts. The products are characterized by means of IR and ^{1}H-NMR spectroscopy, GPC, viscometry, and light scattering. Hydrogenation proceeds without destruction and selectively for olefinic unsaturation. The hydrogenated copolymers are homogeneous in molecular weights and chain composition. The influence of the copolymer structure on the solution properties in selective solvents is established. In cyclohexane an equilibrium between micelle associates and individual polymer coils, monomolecular micelles, or micelle aggregates are observed, depending on the type of the copolymer. The micellization in base-lubricating oil leads to micelle fractions with a different degree of association.

INTRODUCTION

Polystyrene–poly(ethylene propylene) block copolymers behave like thermoplastic elastomers[1] and good viscosity index improvers for lubricating oils.[2] Generally these copolymers are obtained by olefin hydrogenation of styrene–isoprene block copolymers with a well-defined structure. The hydrogenation of polymers in the presence of heterogeneous catalysts is difficult and generally unsatisfactory. Homogeneous metal–organic hydrogenation catalysts are more effective and useful for the polydiene moiety under mild conditions.[3-5] The difficulties in homogeneous hydrogenation are associated with removing of the traces of catalysts.

This paper deals with the effect of the selective hydrogenation of styrene–isoprene block copolymers with different chain structures on their solution properties.

EXPERIMENTAL

Hydrogenation

The synthesis and the characterization of styrene–isoprene block copolymers with different structures have been described in a previous paper.[6] Diblocks (I–S and I–(I/S)–S), tapered with long (I/S–TL) and short (I/S–TS) blocks and random (I/S–R) copolymers were hydrogenated.[7]

The solution of the polymer sample (10 wt %) was charged in a 2L-autoclave (Büchi-BEP 280) purged with purified argon. The catalysts composed of nickel 2-ethyl hexanoate and triisobutyl aluminium or nickel acetylacetonate with nickel capronate and triisobutyl aluminium were previously prepared in cyclohexane at 40°C under hydrogen. The catalyst was added to the polymer solution and hydrogen was bubbled through the reactor at a constant hydrogen pressure of 50 psi. The hydrogenation continued 12–16 h at 80–100°C under efficient stirring. The removing of the catalyst traces from the copolymer solution was carried out by complexing with dimethylglyoxime[8] or salt formation with oxalic acid.[9] The polymer was precipitated in cold methanol.

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[*] To whom correspondence should be addressed.

[†] Department of Mineral Oils, Petrochemical Combinate, Pleven, Bulgaria.

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Table I Hydrogenation of a Diblock Styrene–Isoprene Copolymer with Homogeneous Catalysts

		GPC Analysis Before the Hydrogenation			Hydrogenation Conditions					GPC Analysis after the Hydrogenation		
					Catalyst							
No.	Sample	$\bar{M}_w$ (g/mol)	$\bar{M}_n$ (g/mol)	MWD	Type	Ni : Al (Molar Ratio)	T (°C)	p_{H_2} (psi)	Degree of Hydrogenation (%)	$\bar{M}_w$ (g/mol)	$\bar{M}_n$ (g/mol)	MWD
1	I–(I/S)–S	54,000	44,900	1.20	Nickel acetylacetonate/triisobutyl-aluminum	1 : 50	100	50	95	54,150	47,100	1.15
2	I–(I/S)–S	54,000	44,900	1.20	Nickel acetylacetonate + nickel capronate/triisobutyl aluminium	1 : 5.4	80	40	100	54,120	45,000	1.20
3	I–(I/S)–S	54,000	44,900	1.20	Nickel-2-ethylhexanoate/triisobutyl aluminium	1 : 4.3	90	50	98	54,160	46,200	1.17

Table II Dependence of the Solubility of the Hydrogenated Poly(Styrene–Isoprene) Diblock Copolymer from the Degree of Hydrogenation

							Solubility (g/100 mL Solvent at 25°C)	
No.	Copolymer	Wt % of Polystyrene[a]	$\bar{M}_w$ (g/mol)[b]	$\bar{M}_n$ (g/mol)[b]	MWD[b]	Degree of Hydrogenation[c] (%)	Cyclohexane	Base Lubricating Oil
1	I–S	36	102,100	74,800	1.36	50	3.05	Unsoluble
2	I–S	36	102,100	74,800	1.36	80	4.29	4.27
3	I–S	36	102,100	74,800	1.36	100	5.02	5.10

[a] Determined from^{1}H-NMR analysis.

[b] Determined by GPC.

[c] Determined from IR and ^{1}H-NMR analyses.

Characterization

The hydrogenation was followed by IR (Spectrophotometer Specord M 80, Carl Zeiss) and ^{1}H-NMR analysis (250 MHz Bruker Spectrospin NMR spectrometer, chloroform as a solvent and tetramethylsilane as an internal reference).

Molecular weights and polydispersity of the copolymers were measured by GPC [Waters 150C apparatus equipped with five ultraStyragel columns of 100,500,500, 10^3, and 10^4 Å pore size, tetrahydrofuran eluent, flow rate 1.0 mL/min, polystyrene calibration, temperature 45°C, RI and UV (254 nm) detectors].

The solution properties of the block copolymers were determined by methods of viscometry and light scattering. The intrinsic viscosity was measured using standard Ubbelohde viscometers.

Light scattering measurements were made on a PhotoGonio-Diffusiomètre FICA (France) in unpolarized light, $\lambda = 546$ nm, 25 ± 1°C. The instrument was calibrated using pure benzene. The solvents (chloroform, toluene, tetrahydrofuran, cyclohexane) were of analytical purity grade; they were dried and distilled several times before use. The copolymer solutions were clarified by filtration through a system of fritted glass filters.

The base lubricating oil used in this study was paraffinic oil. The solutions were prepared by dissolving of the copolymers in the oil at 70–100°C with stirring during 12 h. The base lubricating oil was subjected to the same heating. The solutions and the neat base oil were filtered through Millipore filters of a pore size of 0.45×10^3 and 0.25×10^3 nm under argon.

The refractive index increments were measured using a Pulfrich refractometer with a divided cell.

RESULTS AND DISCUSSION

IR and ^{1}H-NMR analyses show that the hydrogenation proceeds completely (95–100%) and selectively for olefinic unsaturation. The hydrogenated copolymers checked by GPC have unchanged molecular weight and MWD as precursors. After the purification with dimethylglyoxime or oxalic acid, the

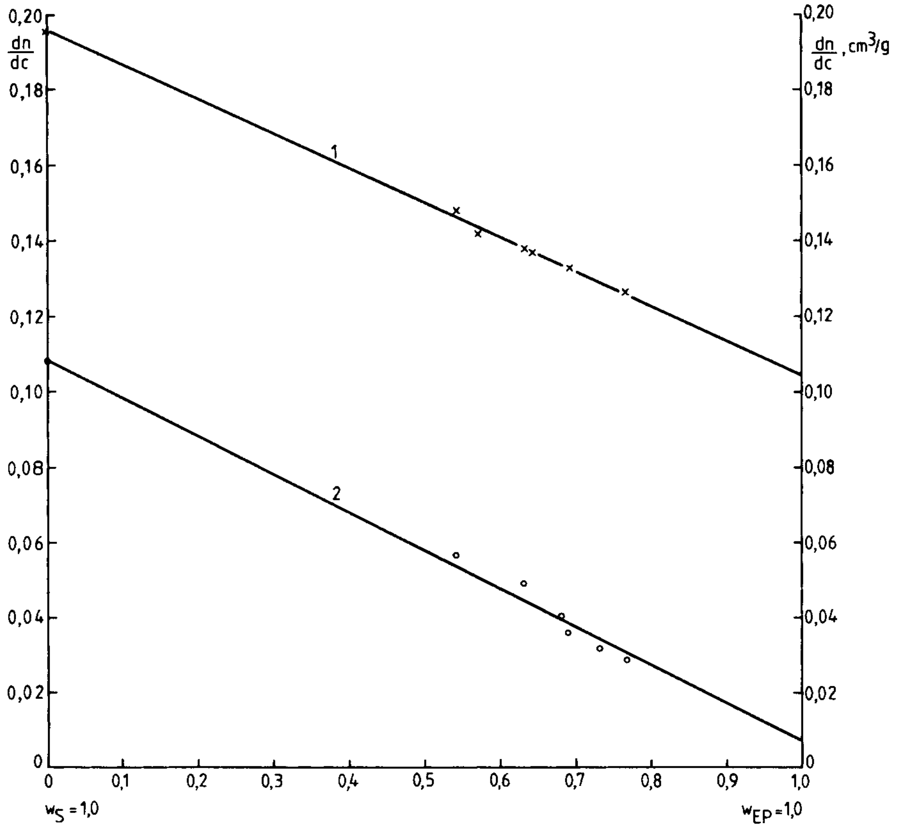

Figure 1 Dependence of the refractive index increments on the copolymer composition in: (1) tetrahydrofuran; (2) toluene.

Table III Molecular Weights of Polystyrene–Poly(Ethylene–Propylene) Copolymers Determined by Light Scattering

		THF	Chloroform	Toluene
No.	Copolymer	$\bar{M}_{app} \times 10^{-4}$ (g/mol)	$\bar{M}_{app} \times 10^{-4}$ (g/mol)	$\bar{M}_{app} \times 10^{-4}$ (g/mol)
1	EP-S	11.60	9.90	8.72
2	EP/S-TL	12.20	9.30	11.70
3	EP/S-TS	6.90	6.40	8.00

traces of nickel in the polymers is about 0.4 ppm (determined by atomic absorption analysis).

The conditions for selective and complete hydrogenation are found using three catalyst systems (Table I). The combination of two organonickel compounds leads to synergistic effect—more complete hydrogenation at more mild conditions. The influence of the copolymer chain structure on the degree of hydrogenation is negligible.

The degree of hydrogenation reflects on the solubility of the copolymers in selective solvents. This influence is most obvious in the case of diblock copolymers (Table II).

The dependence of the refractive index increments on the copolymer composition in tetrahydrofuran and toluene (Fig. 1) allows us to obtain by extrapolation the values of the refractive index increment of alternating ethylene-propylene copolymer in solvents in which this copolymer is unsoluble. The following values are obtained: $(dn/dc)_{PEP} = 0.102$ and 0.0036 in tetrahydrofuran and toluene, respectively. The values of $\bar{M}_{app}$ determined in a variety of solvents are represented in Table III.

Unfortunately, we did not cover a sufficiently wide range of refractive index increments to thoroughly investigate the heterogeneity of composition. Therefore, GPC analyses of the copolymers are performed using two detectors (RI and UV at 254 nm) and tetrahydrofuran as an eluent (Table IV). The results show narrow MWD, typical for living anionic polymerization, and GPC curves of RI and UV detection completely coincide. The values of $\bar{M}_{app}$ determined by light scattering in THF and that of $\bar{M}_w$ from GPC are very closed so that it might be correct to use for $\bar{M}_w$ the values obtained by GPC. The combination of these methods allows us to consider that the products investigated are homogeneous in chain composition even after hydrogenation.

Determination of R_θ as a function of the concentration and the angle for the investigated copolymers was performed in cyclohexane and base lubricating oil, selective solvents for PEP blocks, at 25°C. The plots of K_c/R_θ versus c and $\sin^2 \theta/2 + kc$ (Zimm plots) for the copolymers in cyclohexane are with complex shape and it is difficult to explain these dependences. This is seen even in Figures 2 and 3 for the plots K_c/R_θ versus c for copolymers with different microstructure. The shape of the curves and the values of $\bar{M}_w$ determined (Table V, nos. 1, 2, 3, and 6) indicate an equilibrium between individual

Table IV Molecular Weights Values for Polystyrene–Poly(Ethylene–Propylene) Copolymers from Light Scattering and GPC

		Light Scattering (in THF)	GPC Analysis			
No.	Sample	$\bar{M}_{app} \times 10^{-4}$ (g/mol)	$\bar{M}_w \times 10^{-4}$ (g/mol)	$\bar{M}_n \times 10^{-4}$ (g/mol)	MWD	$\frac{\bar{M}_{app}}{\bar{M}_w{}^a}$
1	EP-S	11.6	10.21	7.48	1.36	1.14
2	EP-(EP/S)-S	5.6	5.42	4.71	1.15	1.03
3	EP/S-TL	12.2	12.08	9.83	1.23	1.01
4	EP/S-TS	4.93	4.93	4.80	1.03	1.00
5	EP/S-R	13.63	12.39	9.91	1.25	1.10

[a] Determined by GPC.

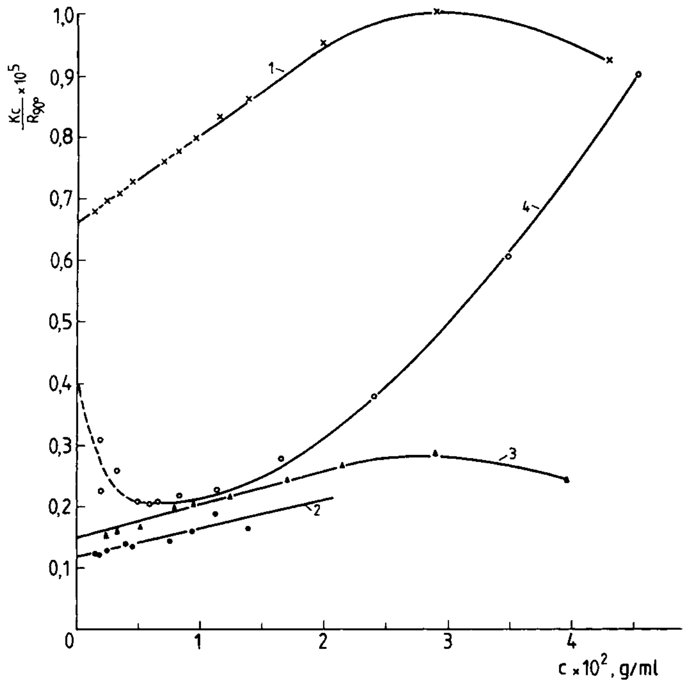

Figure 2 Dependence of $K_c/R_{90°}$ on the concentration in cyclohexane: (1) EP–S; (2) EP–(EP/S)–S; (3) EP/S–TL; (4) EP/S–R.

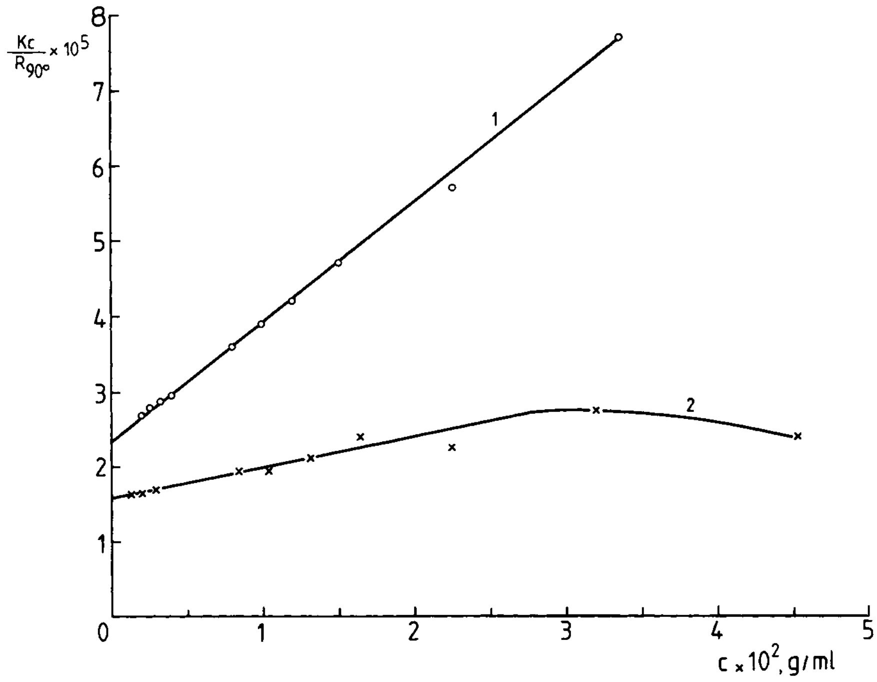

Figure 3 Dependence of $K_c/R_{90°}$ on the concentration in cyclohexane: (1) EP/S–TS (no. 4 from Table V); (2) EP/S–TS (no. 5 from Table V).

Table V Intrinsic Viscosity and Light Scattering Data for Polystyrene–Poly(Ethylene–Propylene) Block Copolymers

			THF			Chloroform					Base Lubricating Oil				
									Z					Z	
No.	Copolymer	Wt % of Polystyrene[a]	$[\eta]$ (dL/g)	$\bar{M}_{app} \times 10^{-4}$ (g/mol)	$\frac{dn}{dc}$	$[\eta]$ (dL/g)	$\bar{M}_{app} \times 10^{-4}$ (g/mol)	$\frac{dn}{dc}$	$(c = 0)$	$(c > 0)$	$[\eta]$ (dL/g)	$\bar{M}_{app} \times 10^{-4}$ (g/mol)	$\frac{dn}{dc}$	$(c = 0)$	$(c > 0)$
1	EP-S	36	—	11.6	0.135	—	15.15	0.112	3.4	5.3	Transparent over 160°C				
2	EP-(EP/S)-S	36	—	5.6	0.137	—	84.75	0.112	7.7		0.37	848.00	0.036	1.4	1.7
3	EP/S-TL	43	0.85	12.2	0.142	0.71	21.70[b]	0.016[b]			0.60	1250.00	0.036	1.0	1.4
4	EP/S-TS	31	0.55	6.9	0.133	0.43	7.00	0.112	1.2	1.9	0.36	24.39	0.036	1.4	2.5
5	EP/S-TS	46	0.27	4.93	0.148	0.20	6.29	0.112	2.2	4.4	0.24	27.78	0.036	1.0	1.1
6	EP/S-R	37	0.44	13.63	0.138	0.31	66.23	0.110	2.6	3.2	Transparent at 115°C				

[a] Determined from ^{1}H-NMR analysis.

[b] In toluene.

polymer coils and multimolecular micelles. This equilibrium is more obvious for EP/S-R (Fig. 2, curve 4) where the curve turns sharply upwards at lower concentrations. In the solutions of diblock (Fig. 2, curves 1 and 2) and tapered (EP/S-TL) (Fig. 2, curve 3) copolymers predominantly micelles exist. The plots for tapered copolymers with short blocks (Fig. 3) give values for $\bar{M}_w$ (Table V nos. 4 and 5) near to these obtained in THF so that it can be assumed that they do not aggregate into micelles independently of the copolymer composition. Probably a major number of ethylene–propylene blocks protect sufficiently the unsoluble styrene blocks barring the association so that monomolecular micelles are formed, as some decrease in intrinsic viscosity appears (Table V).

The dependences of $K_c/R_{90°}$ versus c for the copolymers in lubricating oil are plotted in Figures 4 and 5. Unfortunately, data for ideal and random copolymers are not included because their solutions are transparent at 160 and 115°C, respectively. All copolymers are aggregated into micelles. The two-step shape of the curves for diblock copolymers (Fig. 4, curve 1) and copolymers tapered with long blocks (Fig. 4, curve 2) indicates the existence of polymolecular micelles with different degrees of aggregation.

The formation of polymolecular micelles is confirmed from the decrease of the intrinsic viscosity with changing the solvent from good to selective (Table V).

In cyclohexane solutions the dissimetry for all copolymers is significant ($Z = R_{45}/R_{135} \approx 3$–$8$) while in base lubricating oil $Z \approx 1.1$–1.4, indicating compact particles (Table V).

The reduction in viscosity with the temperature from −15 to 110°C is negligible, indicating the stability of the micelles in base lubricating oil (Fig. 6).

CONCLUSIONS

Hydrogenation of olefinic unsaturation in styrene–isoprene copolymers is performed completely and without degradation, using homogeneous organometallic catalysts at mild conditions. It is evident by light scattering and GPC that the copolymers with different monomer sequence distribution are homogeneous in molecular weight and chain composition.

The influence of the copolymer structure on the solution properties in cyclohexane is as follows: diblock and tapered copolymers with long blocks pre-

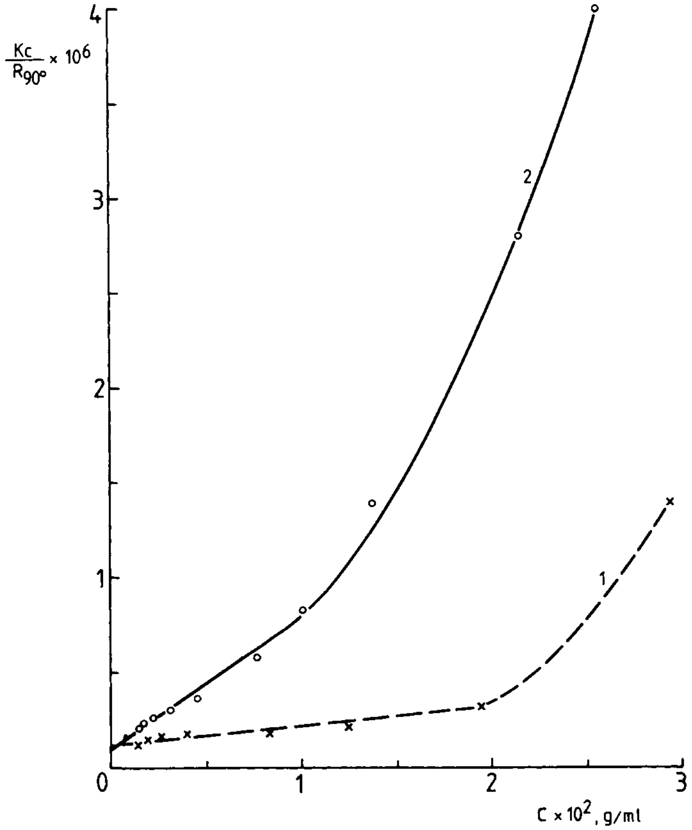

Figure 4 Dependence of $K_c/R_{90°}$ on the concentration in base lubricating oil: (1) EP-(EP/S)-S; (2) EP/S-TL.

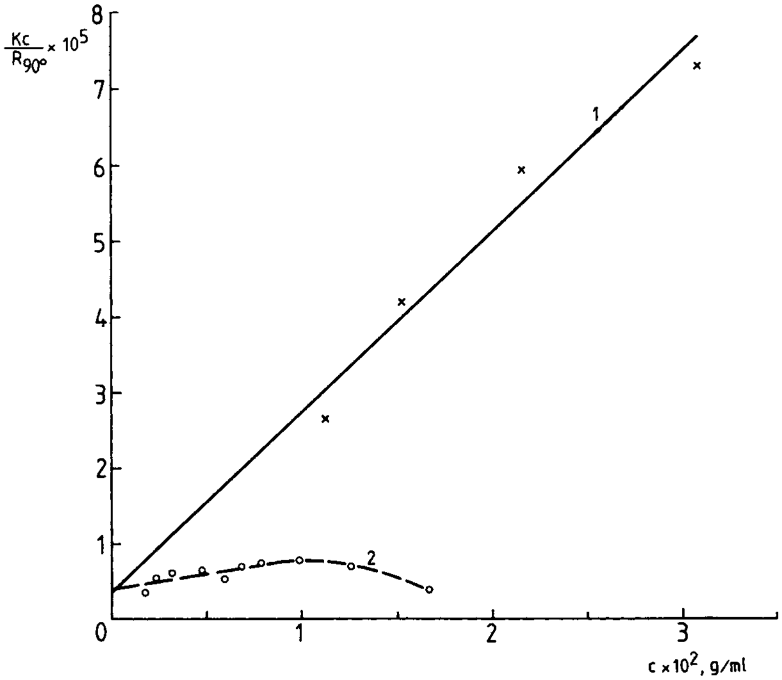

Figure 5 Dependence of $K_c/R_{90°}$ on the concentration in base lubricating oil: (1) EP/S-TS (no. 5 from Table V); (2) EP/S-TS (no. 4 from Table V).

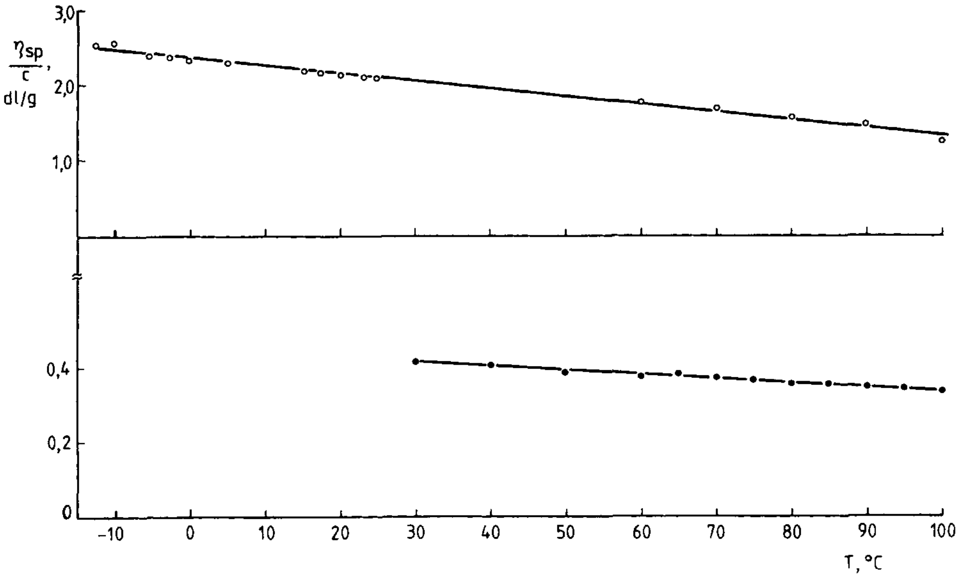

Figure 6 Dependence of the viscosity number on the temperature: (1) EP–(EP/S)–S; (2) EP/S-TL.

dominantly exist as polymolecular micelles; the products with short blocks give monomolecular micelles; in random copolymers solutions an equilibrium between individual copolymer coils and multimolecular micelles exists.

In base lubricating oil all copolymers are aggregated into micelles. The dependence K_c/R_θ versus c indicates the formation of micelles with different degrees of association in the case of diblock and tapered copolymers with long blocks.

The comparison of the solution properties of the hydrogenated poly(styrene–isoprene) products and their parent copolymers[6] show the existence of a larger molecular association in the solutions of hydrogenated polymers. At the same time the solubility of the hydrogenated products in base lubricating oil is higher.

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