ELSEVIER

S0032-3861(96)00173-5

Polymer Vol. 37 No. 16, pp. 3611–3614, 1996

0032-3861/96/$15.00+0.00

Miscibility of associated polymer blends in good solvent: 2. One-end-aminated polystyrene/one-end-sulfonated poly(ethylene glycol) blends in toluene

Mieko Haraguchi, Katsuhiro Inomata and Takuhei Nose*
Department of Polymer Chemistry, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152, Japan
(Received 30 October 1995; revised 20 November 1995)

Compatibility was investigated for blends of one-end-aminated polystyrene (APS) and one-end-sulfonated poly(ethylene glycol) (SPEG) in toluene with changing the association strength and the segment interaction by varying the total polymer concentration. Weight-average molecular weight of APS and SPEG were 5600 and 5700, respectively. Cloud-point concentrations at fixed temperature were measured as a function of the polymer composition. It was demonstrated that the association strength between the amino and sulfonic end groups was strong enough to give two peaks to the misibility gap in the space of solvent volume fraction against the polymer composition, which was theoretically expected for a strong-association system. It was also found that sulfonic groups introduced to PEG chain ends reduced the miscibility of PS and PEG due to association between the sulfonated ends. A Flory–Huggins type theory of associated polymer blend solution could interpret these experimental results qualitatively. Copyright © 1996 Elsevier Science Ltd.

(Keywords: associated polymer blend; compatibility; cloud point)

INTRODUCTION

Associated polymer blends with functional groups can exhibit a wide variety of compatibility and microstructures[1–13]. Polymer blends with functional groups at the chain ends tend to show more regular microstructures than those with functional groups randomly attached on polymer chains. A blend system consisting of two polymers which are able to associate with each other by functional groups at one end of the respective polymer chains may exhibit various types of phase behaviour according to the association strength of the end groups and segmental segregation strength. At the limit of strong association, the blend is like a mixture of block copolymer and homopolymer, while at the limit of weak association it is like an ordinary polymer blend. A strongly associated blend may have a two-peak phase diagram with a deep sharp minimum at the stoichiometric composition where no macroscopic phase separation can occur[13].

In our previous paper[14], we studied miscibility of blend solutions of one-end-aminated polystyrene (APS) and one-end-carboxylated poly(ethylene glycol) (CPEG) with changing the association strength and the segment interaction by varying the total polymer concentration. Cloud points were measured for various combinations of PS or APS and PEG or CPEG. It has been revealed that associations between amino and carboxyl groups enhance the miscibility of PS and PEG. However, the two-peak phase diagram, which is theoretically expected for a strong-association system, was not observed. This is probably because the association between amino and carboxyl ends is not strong enough.

In this study, we take one-end-sulfonated poly(ethylene glycol) (SPEG) as a counterpart of APS to realize a more strongly associated blend than the previous one, and study its miscibility in solution to see whether it exhibits the two-peak phase diagram. Discussion will be made with the aid of the mean-field theory of associated polymer blend solutions used in the previous paper.

EXPERIMENTAL

Samples

Polystyrenes (PS) were products of Pressure Chem. Co. and Toso Co. with narrow molecular weight distribution. Poly(ethylene glycol) (PEG) with methyl ether at one end was a product of Aldrich Co. One-end-aminated polystyrene (APS) was synthesized by amination of the living end of anionically polymerized PS[15]. PEG with a sulfonic group at one end (SPEG) was made by sulfonation of the hydroxyl group at one end of the PEG[16]. Weight-average molecular weight, M_w, polydispersity index, M_w/M_n, and functionality of the samples with code names are listed in *Table 1*.

Toluene for use as solvent was purified by fractional distillation.

Blend solutions were prepared by mixing the two polymers and the solvent in a glass tube, followed by frame-sealing under mild vacuum or by sealing at the top

---

* To whom correspondence should be addressed

Table 1 Characteristics of the samples

Samples	Codes	M_w^a	M_w/M_n^b	Func.[c]	P^d
Polystyrene	PS6	6200	1.04		52
One-end-aminated	APS6	5600	1.06	1.00	47
Poly(ethylene glycol)	PEG6	5700	1.05		46
One-end-carboxylated	CPEG6	5700	1.05	0.96	46
One-end-sulfonated	SPEG6	5700	1.05	0.99	46

[a] M_w was determined by M_n with M_w/M_n, where M_n was measured by vapour pressure osmometry

[b] M_w/M_n was determined by size exclusion chromatography

[c] Functionalities of amino, carboxyl and sulfonyl groups

[d] Degree of polymerization, corresponding to fN or $(1\text{-}f)N$ in the theoretical treatment, defined by [molar volume of polymer]/[molar volume of toluene]

of the tube with a Teflon sheet fixed by a screw in a metal holder. The blend solution was homogenized by vibrating the glass tube with a mixing machine in the one-phase region. For less viscous blend solutions, the intensity of the scattered light from the samples under cooling was measured to determine the cloud point. Solvent concentration, $C_{s,cl}$, at the cloud point, which is here referred to as cloud solvent concentration, was determined at 90°C. Details of experimental procedures have been described in the previous paper[14]. Light scattering was not applied to APS/SPEG blend solutions since the solutions had low cloud solvent concentrations and were very viscous so that clouding by phase separation was slow. Therefore, for the APS/SPEG solutions, the cloud point was determined visually: keeping a sample at a fixed temperature of 80°C for 2 h, we judged transparency by eye to classify the sample as clear, slightly cloudy, and very cloudy. (The cloud solvent concentration, $C_{s,cl}$, was determined by light scattering at 90°C, the same temperature as in the previous study. SPEG is degradable at higher temperatures; 80°C was taken as a temperature where degradation was negligible in the visual long-term experiments of APS/SPEG solutions. Fortunately, the temperature dependence of $C_{s,cl}$ was so small that the difference in experimental temperature is not serious in the present study.)

Solvent concentration and polymer composition as weight fractions were transformed to volume fraction with density data in the literature[17-19].

Experimental results of cloud points will be illustrated as a quasi-binary presentation. Namely, cloud solvent concentrations, $\phi_{s,cl}$, as volume fractions were plotted against volume fraction, Φ_{PEG} (or Φ_{SPEG}), of PEG (or SPEG) in total polymers. Denoting the volume of component X as v[X], they were defined as $\phi_{s,cl} = v$[toluene]/v[total blend solution] and $\Phi_{PEG} = v$[PEG]/v[total polymers] (or $\Phi_{SPEG} = v$[SPEG]/v[total polymers]).

RESULTS AND DISCUSSION

Cloud-point curve

Figure 1 shows cloud points of PS6/SPEG6 with those of PS6/CPEG6. It has been demonstrated in the previous paper[14] that one-end-carboxylated PEG (CPEG) substantially become dimers by association at the chain ends, reducing miscibility with PS. Similarity in $\phi_{s,cl}$ between SPEG and CPEG seen in *Figure 1*, therefore, suggests the presence of association of sulfonated ends.

Figure 2 shows cloud points for APS6/SPEG6 for which strong associations between APS and SPEG are expected. This blend has a high miscibility with cloud solvent concentration being about 30–40%, exhibiting a two-peak cloud-point curve with the highest miscibility around the stoichiometric composition $\Phi_{PEG} = 0.5$. In contrast, no such two-peak phase boundary has been observed in APS/CPEG blend solutions, mainly because of a weak association between amino and carboxyl groups[14].

Analysis with Flory–Huggins type mean-field theory

Enhancement of the miscibility at stoichiometric composition and the possibility of microphase formation in associated polymer blends were first theoretically predicted by Tanaka and co-workers[13]. In the previous paper[14], we extended the theory to describe the miscibility of associated polymer blend *solutions*, and evaluated the free energy of mixing in the framework of Flory–Huggins type mean-field theory. The solution can be regarded as a mixture of free polymer chains and associated polymer chains in thermodynamically good solvent. Under the quasi-binary approximation, the

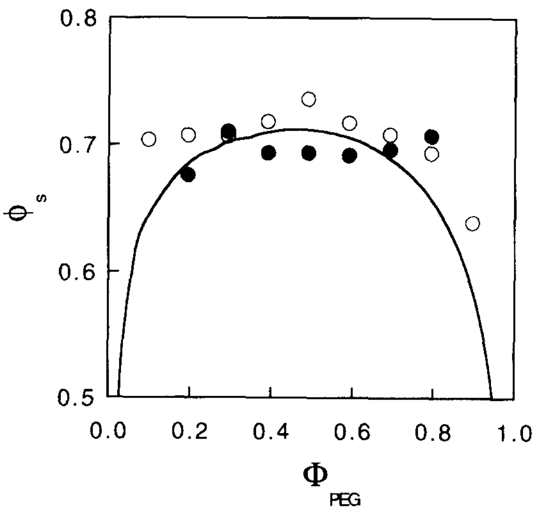

Figure 1 Quasi-binary presentation of cloud points for PS6/CPEG6 (○) and PS6/SPEG6 (●) at 90°C, and comparison of calculated and experimental phase boundaries for evaluation of K_{aa}. , Calculated with $\chi = 0.112$ and $K_{aa} = 36$. $fN = 46$; $(1-f)N = 52$

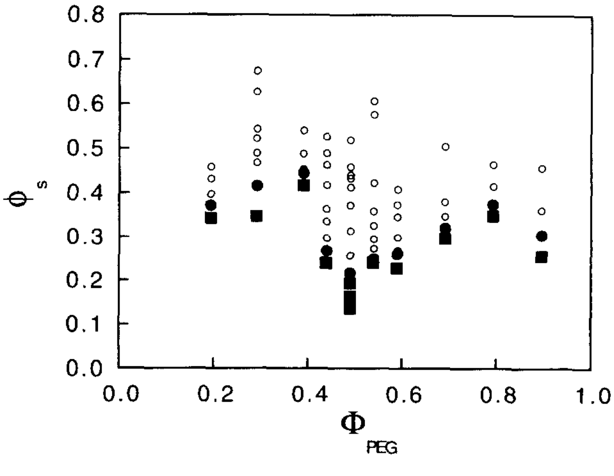

Figure 2 Quasi-binary presentation of cloud points for APS6/SPEG6 at 80°C: (○) clear; (●) slightly cloudy; (■) very cloudy, after 2 h

effective part of free-energy, ΔF_{eff}, for determining the phase equilibrium can be written as[14]:

$$
\begin{aligned}
[\Delta F] &= \frac{N\Delta F_{eff}}{\phi MkT} \\
&= \frac{\theta_a \ln\theta_a}{f} + \frac{\theta_b \ln\theta_b}{1-f} \\
&\quad + \left(\frac{\phi}{2}\right)\left\{\frac{K_{aa}\theta_a^2(1+2\ln\theta_a)}{f} + \frac{K_{bb}\theta_b^2(1+2\ln\theta_b)}{1-f}\right. \\
&\quad \left. + 2K_{ab}\theta_a\theta_b(1+\ln\theta_a\theta_b)\right\} \\
&\quad + \phi N\chi\Phi_a\Phi_b
\end{aligned} \tag{1}
$$

with

$$\theta_a + \phi K_{aa}\theta_a^2 + f\phi K_{ab}\theta_a\theta_b = \Phi_a \tag{2}$$

$$\theta_b + \phi K_{bb}\theta_b^2 + (1-f)\phi K_{ab}\theta_a\theta_b = \Phi_b = 1 - \Phi_a \tag{3}$$

where M is the number of total sites of the system, N is the sum of polymeric indices of polymers a and b, and the polymeric index of polymer a is given by fN. Volume fraction of total polymers of a and b in the solution is $\phi(=1-\phi_s)$, and the fraction of a-polymers in the total polymers is Φ_a. Fractions θ_x and θ_{xy} of the x-polymers are those dissolved as free chains and those associated with y-polymer chains, respectively (x, y = a, b). χ is the segment–segment interaction parameter between polymers a and b, and K_{xy} is association constant for x–y pairs. Details of the derivations have been described in the previous paper.

For a system with N, f, χ and K_{xy}, the free energy of mixing is given as a function of Φ_a and ϕ_s, so that Φ_a of coexisting phases for a fixed ϕ_s can be determined by a conventional method of thermodynamics. Calculations with changing ϕ_s yield the coexisting curve, Φ_a vs. ϕ_s. Fractions of free chains and associated chains are also calculated by equations (2) and (3) for a given solution. Hereafter, polymer a is assigned to SPEG (or PEG) and polymer b to APS (or PS).

Polymeric indices were given as the ratio of molar volume of polymers to molar volume of toluene, shown in *Table 1*, so that the χ parameter was per site, the size of which was the volume of a toluene molecule.

In the previous paper, we determined the χ parameter to be 0.112 for PS and PEG, which described the miscibility of PS and PEG quite well. Using this χ value, the theory well described the phase behaviour of PS/CPEG and APS/CPEG associated solutions with association constants $K_{aa} = 480$ for CPEG–CPEG and $K_{ab} = 53$ for APS–CPEG. To determine K_{aa} for a sulfonated-end pair, the fitting to the data of PS6/SPEG6 was made with $\chi = 0.112$ and K_{aa} as a parameter. Comparison of the fitted curve and experimental values are presented in *Figure 1*. The obtained association constant is $K_{aa} = 36$ for SPEG–SPEG, which is smaller than that for CPEG–CPEG, although the accuracy of K_{aa} value determination was generally bad[14].

With these values of χ and K_{aa}, coexistence curves were calculated for APS6/SPEG6 by varying the K_{ab} value to try to reproduce the observed cloud-point curve; they are shown in *Figure 3*. Here K_{bb} is assumed to be zero because there is no association between the amino ends[14]. The calculated curves do not give a two-peak phase diagram as observed. A strong a–b association, which is needed for the dip in the phase diagram at the stoichiometric composition, makes the blend too miscible to exhibit phase separation. In order to make the blend phase-separate with strong a–b association, the segment interaction parameter χ should be larger, which leads to phase separation. Actually, if the χ value was taken to be larger, $\chi = 0.2$ for instance, the calculated coexistence curve has two peaks, as shown in *Figure 4*, reproducing the experimental observation. For this set of parameters, fractions of free chains and associates and the free energy profile at $\phi_s = 0.2$ were calculated as a function of SPEG composition, as presented in *Figures 5* and *6*, respectively.

At $\phi_s = 0.2$, where a one-phase region exists around 50% SPEG composition between two-phase regions, the a–b associate fraction dominates over other fractions around 50% SPEG. As a consequence, the free energy has a shallow dip there, and is able to have two common tangential lines, resulting in the two two-phase regions.

Because of the association between sulfonated ends, the phase boundary must theoretically be asymmetric, having a higher peak at a higher SPEG composition. But

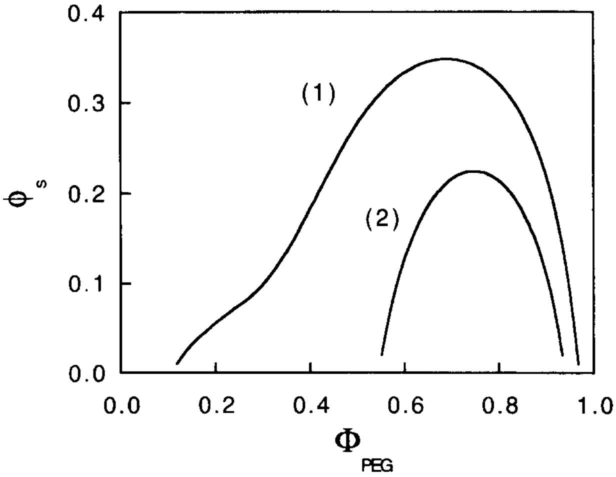

Figure 3 Calculated coexistence curves for APS6/SPEG6 [$fN = 46$; $(1-f)N = 47$] with $\chi = 0.112$, $K_{aa} = 36$ and (1) $K_{ab} = 80$ or (2) $K_{ab} = 500$

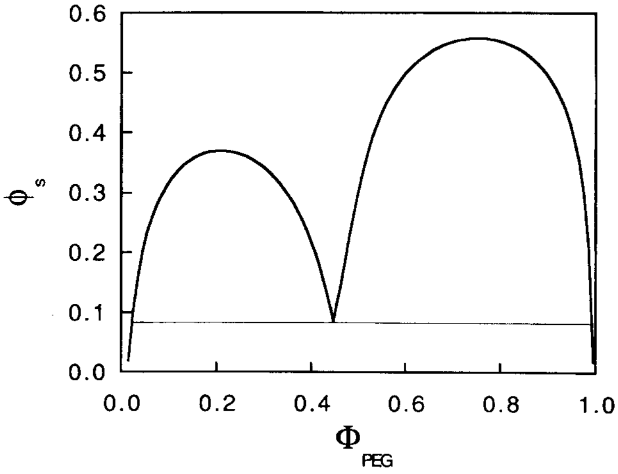

Figure 4 Calculated coexistence curves for APS6/SPEG6 [$fN = 46$; $(1-f)N = 47$] with $\chi = 0.2$, $K_{aa} = 36$ and $K_{ab} = 700$

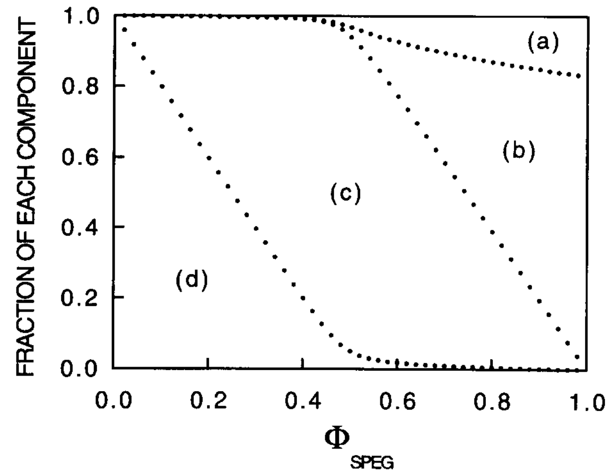

Figure 5 Fractions of free and associated polymer chains for APS6/SPEG6 [$fN = 46$; $(1-f)N = 47$] at $\phi_s = 0.2$, with $\chi = 0.2$, $K_{aa} = 36$ and $K_{ab} = 700$. (a) Free SPEG θ_a; (b) SPEG–SPEG associates θ_{aa}; (c) SPEG–APS associates θ_{ab}; (d) free APS θ_b

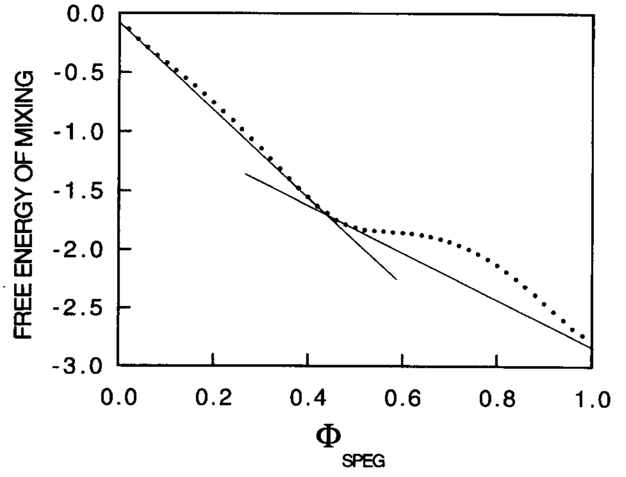

Figure 6 Free energy of mixing for APS6/SPEG6 [$fN = 46$; $(1-f)N = 47$] at $\phi_s = 0.2$, with $\chi = 0.2$, $K_{aa} = 36$ and $K_{ab} = 700$. Tangential lines indicate equality of chemical potentials in coexisting phases, with tangential points showing the polymer compositions of the coexisting phases

actually the blends with lower SPEG content are rather less miscible than those with higher content (*Figure 2*).

The theory is not so satisfactory in describing the experimental observation. The theory requires the χ value to be larger than that estimated from the miscibility of PS/PEG blend solution, and also fails in describing the asymmetry of the miscibility. These disagreements between the theory and the experiment can be attributed to the dependence of χ on solvent concentration and polymer composition. However, a more important issue in the theoretical interpretation is that the theory supposes no mesophase formation but assumes random mixing. In a system of strong associations between polymers a and b, the system around the stoichiometric composition must behave like a diblock copolymer, possibly forming a mesophase of ordered structure. A diblock copolymer corresponding to strongly associated APS–SPEG of the present system is supposed to have the polymeric index $N = 47 + 46 = 93$, and the segregation strength $N\chi = 10$–20 in the bulk (for $\chi = 0.112$–0.2), which implies that $N\chi(1-\phi_s) = 8$–16 in solution of $\phi_s = 0.2$. Since the critical segregation strength for mesophase formation is theoretically predicted to be about 15, the present associated blend may form a mesophase around the stoichiometric composition in the concentrated region. (According to the BLFH theory[20–22], the segregation strength $(N\chi)_{\mathrm{ODT}}$ at order–disorder transition for $f = 0.5$ is given by $(N\chi)_{\mathrm{ODT}} = 10.495 + 41.0N^{*-1/3}$, with N^* being defined as $N^* = Na^6v^{-2}$, where a is segment length and v is segment volume. N^* can be rewritten as $N^* = N[(\langle r^2\rangle/M)M_0]^3/(V_sM_0/N_A)^2 = MN_A^2(\langle r^2\rangle/M)^3/V_s^2$, with $\langle r^2\rangle$ being the mean square end-to-end distance of unperturbed chain, M the molar mass, V_s the specific volume of polymer, N_A the Avogadro constant, and M_0 segment molar mass. One obtains $N^*/M = N_A^2(\langle r^2\rangle/M)^3/V_s^2 = 0.035$ for PS and 0.074–0.15 for PEG[23]. Therefore, N^* of the present case ($M = 5600 + 5700$) is estimated to be 400–1700, which gives $(N\chi)_{\mathrm{ODT}} = 13$–$16$.) The presence of the mesophase must change the phase diagram. Nonrandom mixing near the mesophase may give a discrepancy from theoretical prediction of the present treatment even in the disordered phase. Actually small-angle X-ray scattering suggests the presence of a mesophase in the present blend near the stoichiometric composition. Details of the study will be reported elsewhere.

ACKNOWLEDGEMENT

The authors thank Professor Nakahama of Tokyo Institute of Technology for providing the functional polymers used in this study.

REFERENCES

1 Eisenberg, A., Smith, P. and Zhou, Z.-L. *Polym. Eng. Sci.* 1982, **22**, 1117
2 Smith, P. and Eisenberg, A. *J. Polym. Sci., Polym. Lett. Edn* 1983, **21**, 223
3 Zhou, Z.-L. and Eisenberg, A. *J. Polym. Sci., Polym. Phys. Edn* 1983, **21**, 595
4 Pugh, C. and Percec, V. *Macromolecules* 1986, **19**, 65
5 Vivas de Meftahi, M. and Fréchet, J. M. *Polymer* 1988, **29**, 477
6 Iwasaki, K., Tokiwa, T., Hirao, A. and Nakahama, S. *New Polym. Mater.* 1993, **4**, 53
7 Horrion, J., Jérôme, R. and Teyssié, Ph. *J. Polym. Sci., Polym. Lett. Edn* 1986, **24**, 69
8 Horrion, J., Jérôme, R. and Teyssié, Ph. *J. Polym. Sci., Polym. Chem. Edn* 1990, **28**, 153
9 Russell, T. P., Jérôme, R., Charlier, P. and Foucart, M. *Macromolecules* 1988, **21**, 1709
10 Iwasaki, K., Hirao, A. and Nakahama, S. *Macromolecules* 1993, **26**, 2126
11 Tanaka, F. *Macromolecules* 1989, **22**, 1988
12 Tanaka, F. *Macromolecules* 1990, **23**, 3784, 3790
13 Tanaka, F., Ishida, M. and Matsuyama, A. *Macromolecules* 1991, **24**, 5582
14 Haraguchi, M., Nakagawa, T. and Nose, T. *Polymer* 1995, **36**, 2567
15 Ueda, K., Hirao, A. and Nakahama, S. *Macromolecules* 1990, **23**, 939
16 Iwasaki, K. Doctor Thesis, Tokyo Institute of Technology, 1993
17 Höcker, H., Blake, G. J. and Flory, P. J. *Trans. Faraday Soc.* 1971, **67**, 2251
18 Mandelkern, L. *J. Appl. Phys.* 1955, **26**, 443
19 Tsujita, Y., Nose, T. and Hata, T. *Polym. J.* 1973, **5**, 201
20 Leibler, L. *Macromolecules* 1980, **13**, 1602
21 Fredrickson, G.H. and Helfand, E. *J. Chem. Phys.* 1987, **87**, 697
22 Brazovskiĭ, S. A. *Sov. Phys. JETP* 1975, **41**, 85
23 Huglin, M. B. in 'Polymer Handbook' (Eds J. Brandrup and E. H. Immergut), 3rd edn, Wiley, New York, 1989, Ch. 7, p.1