NETWORK FORMATION IN POLYMERIC MEDIA AND SOME NETWORK PROPERTIES

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ABSTRACT

The following network copolymers have been synthesized and examined: PVTCA–PMMA, PVTCA–PSt, PVBA–PMMA, PVTCA–PCP (PVTCA–polyvinyl trichloroacetate, PMMA–polymethyl methacrylate, PSt–polystyrene, PVBA–polyvinyl bromacetate, PCP–polychloroprene). The synthetic routes utilized the radical-forming reactions between organic halides and organometallic derivatives [$Mn_2(CO)_{10}$, photochemical initiation ($\lambda = 435.8$ nm) at 25°C, $Mo(CO)_6$, thermal initiation at 80°C]; network properties were investigated by dilatometry, n.m.r., torsion pendulum and electron microscopy.

The networks show two-phase behaviour. In the case of PVTCA–PMMA systems one phase consists of an intimate mixture of PVTCA and PMMA chains, while with PVTCA–PSt phase separation into the pure components is more nearly complete.

It is concluded that in the PVTCA–PCP copolymers the size and separation of polychloroprene domains depend on the mean chain length of the PCP segments and the density of crosslinking, respectively.

The two-phase structure of PVBA–PMMA copolymers may be demonstrated directly by electron microscopy without recourse to staining.

The morphology of these networks appears to be determined by the opposition between thermodynamic incompatibility of the component homopolymers and the geometrical constraints arising from the network structure.

1. INTRODUCTION

The properties and morphologies of multicomponent polymer systems are currently of considerable interest, and block copolymers based on styrene and butadiene of the AB and ABA types have attracted particular attention[1]. In this paper we shall be concerned with the synthesis and properties of more complex copolymers, namely networks composed of blocks of different molecular species.

Investigation of the relations between structure and properties requires ideally substances of which the structures are fully determinable—a situation which, unfortunately, is never encountered with synthetic high polymers.

Anionic polymerization has been widely employed in the synthesis of AB and ABA block copolymers, since the relatively narrow (ideally, Poisson) molecular weight distribution obtainable by this technique in favourable
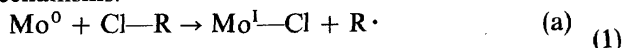
circumstances allows unusually precise control of block length. However, its application is limited, being confined, with few exceptions, to hydrocarbon monomers. On the other hand, free-radical polymerization offers choice from a wider range of components, but suffers from the disadvantage of producing broader distributions. Nevertheless, we believe that interesting correlations between structure and properties can be established by studies of copolymers prepared by free-radical reactions, and we have recently been exploring the possibilities of this approach.

For present purposes, a synthetic route to block and graft copolymers and networks is only of value if it satisfies the following minimal requirements: (i) it must not produce significant quantities of homopolymers, (ii) it should allow calculation of average block lengths and (iii) it should permit calculation of average crosslink or graft densities. In free-radical synthesis of block and network copolymers, a radical attached to a polymer molecule of type A must at some stage propagate with another type of monomer to generate ultimately a block of B, or to form a junction point with a block of B, or it must combine with a radical attached directly or remotely to a polymer chain of type B. The basic problem is therefore to produce 'attached' radicals under conditions which minimize undesirable combination and transfer processes leading to homopolymers. Polymerizing systems can be envisaged which approach this situation when conventional azo or peroxide initiators are used; the crosslinking of dienes by free-radical propagation through their double bonds, or grafting on to preformed polymer by chain transfer fall into this category, provided the relevant mean kinetic chain lengths are sufficiently large. Such systems are special cases, however, and the most general free-radical syntheses of the types of polymer under discussion involve direct production of radicals attached to prepolymer chains in the initiation step. Several methods of doing this have been used, e.g. homolysis of suitable linkages, such as peroxy, incorporated in the backbones or mechanical rupture of the backbones themselves, and redox reactions of hydroperoxide groups attached to polymer chains. Redox reactions are particularly suitable for our purposes since they often give no unattached radicals.
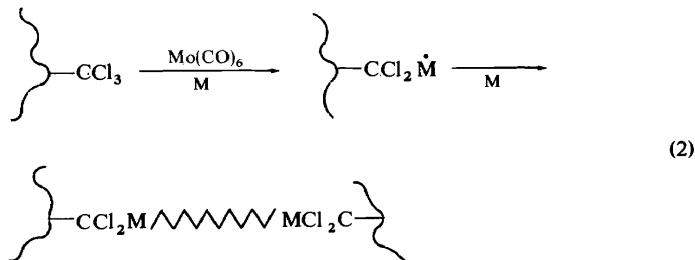
We have utilized the radical-forming reactions between organic halides and complexes of metals in low oxidation states[2] in block copolymer and network syntheses[3-6], and summarize some of our results in the present paper.

2. NETWORK SYNTHESIS AND CHARACTERIZATION

The chemistry of the radical-generating processes has been described elsewhere[2] and will not be reproduced in detail here. A wide variety of organometallic derivatives has been studied, but most of the preparative work has been carried out with molybdenum carbonyl $Mo(CO)_6$, which shows convenient activity at 80°C, and manganese carbonyl $Mn_2(CO)_{10}$, which is an effective photoinitiator ($\lambda = 435.8$ nm) at 25°C. Radical formation is a redox process, following, for example, equations 1a, b, which, however, do not represent reaction mechanisms.

$$Mo^0 + Cl—R \rightarrow Mo^L—Cl + R\cdot \qquad (a)$$
$$Mn_2(CO)_{10} + Cl—R \xrightarrow{h\nu} Mn^I(CO)_5Cl + R\cdot + \tfrac{1}{2}Mn_2(CO)_{10} \quad (b)$$

(1)

Further oxidation of Mo^I up to Mo^V may occur, with additional radical formation[7]. When R is part of a polymer chain, initiation leads directly and entirely to attached radicals. Thus, if the reaction is carried out in the presence of a polymerizable monomer M, block formation occurs, and if the termination reaction in the polymerization of M involves radical combination, a crosslink between two polymer chains is formed, as shown in 2.

$$\text{—CCl}_3 \xrightarrow[\text{M}]{\text{Mo(CO)}_6} \text{—CCl}_2\dot{\text{M}} \xrightarrow{\text{M}}$$

$$\text{—CCl}_2\text{M}\diagup\backslash\diagup\backslash\diagup\backslash\diagup\text{MCl}_2\text{C—}$$

(2)

Clearly, if the prepolymer chains carry a number of halide groups, network formation is possible[3], while if the halide groups are situated only at the ends of prepolymer molecules the product is a block copolymer. The prepolymer chains will carry branches as well as crosslinks if the termination reaction occurs partly by disproportionation. Addition of a chain transfer agent, or a monomeric halide such as ethyl trichloracetate, will lead to the formation of unattached radicals, and hence ultimately to branches on the prepolymer. Some homopolymer of M will also be produced in these circumstances.

This type of synthesis is versatile; the only restriction on the prepolymer is that it should be soluble and carry the required halide groups, and M may be any monomer polymerizable by free-radicals.

The initial rate of initiation I_0 may be derived from observed rates of polymerization of the vinyl monomer under comparable conditions, except that a chemically equivalent monomeric halide is substituted for the prepolymer. This procedure eliminates effects of variation in the termination coefficient arising from gelation or attachment of growing chains to prepolymer molecules. There is considerable evidence[6] that I_0 does not depend on the nature of M. Mean crosslink lengths may be calculated from I_0, $[M]$ and the familiar kinetic parameter $k_p k_t^{-\frac{1}{2}}$. When the conditions are such that k_t is not constant (e.g. at high crosslink density) it is simplest to estimate the mean crosslink length from the conversion of M and the total number of initiating radicals generated. The crosslink density is calculable from the gel-time of the system and the reaction time, since at the gel point the crosslink density corresponds to one crosslinked unit per weight average prepolymer chain. In simple cases, branch: crosslink ratios may be obtained from a knowledge of the relative importance of disproportionation and combination in the termination reaction (i.e. k_{tc}/k_{td}); when chain transfer is significant, or when unattached radicals are generated the calculation is more cumbersome, although conventional. Allowance must be made for initiator consumption during reaction, if this is significant. The relevant procedure has been described in earlier papers[4, 5]; unfortunately, available data do not always allow corrections for consumption to be made with certainty, so that uncertainties in some network parameters are inevitable at present (cf. *Table 1*).

3. PROPERTIES OF NETWORKS

Most of our work has been carried out with polyvinyl trichloracetate (PVTCA) as prepolymer; other prepolymers studied include polyvinyl bromacetate (PVBA), the polycarbonate (I) and cellulose acetate containing a proportion of trichloracetate groups.

$$-\left(-O-\bigcirc-\underset{\underset{CCl_3}{\overset{H}{\underset{|}{\overset{|}{C}}}}}{}-\bigcirc-O-CO-\right)_n$$
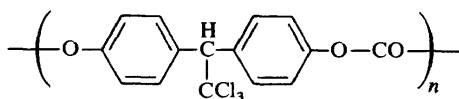
(I)

Methyl methacrylate (MMA), styrene (St) and chloroprene (CP) have been used as vinyl monomers.

3.1 PVTCA–PMMA and PVTCA–PSt networks

3.1.1 *Dilatometric studies*[8]
Nine networks were prepared by the methods outlined. After polymerization, excess monomer was removed under vacuum for 15 h, approximately.
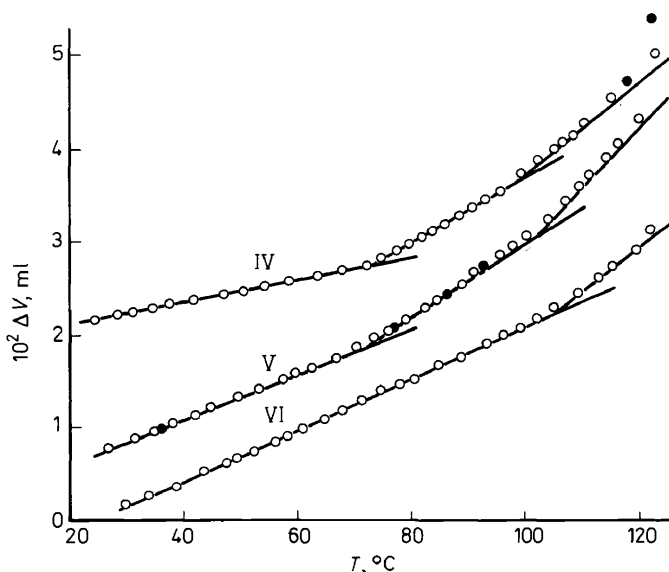

Figure 1. Dilatometric data for networks IV, V, VI (*Table 1*) showing the presence of two glass-transition temperatures (except for VI). ○ represent experimental data; ● represent experimental data for network V after holding the specimen at the indicated temperatures for several hours. Curves below T_{g1} and above T_{g2} calculated from equation 3.

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Polymers were annealed at 100°C in the dilatometer bulbs in high vacuum, before the confining liquid, mercury, was added. Differential dilatometry was used, to eliminate errors arising from temperature fluctuations in the thermostat. Some preparative details and structural characteristics of the networks are given in *Table 1*. Dilatometric observations showed the existence of the

Table 1. Network preparation and structures (PVTCA–PMMA, PVTCA–PSt systems)

Specimen	Vinyl monomer	Mean no. of crosslinked units per weight average prepolymer chain	$\bar{P}_n$ crosslinks	Branch: crosslink ratio
I	MMA	3	4560–4740	4
II	MMA	9	5060–5440	4
III	MMA	16–18	6900–8000	4
IV	MMA	1	11820	10
V	MMA	3·5	12700	10
VI	MMA	7	16760	10
VII	St	1	2880	∼0
VIII	St	3	4750	∼0
IX	St	6	5800	∼0

I–III, VII–IX polymerized at 25°C; $Mn_2(CO)_{10}$ as photoinitiator ($\lambda = 435.8$ nm); IV–VI polymerized at 80°C; thermal initiation by $Mo(CO)_6$; $\bar{P}_w$(PVTCA) $= 2600$.

two glass transitions (temperatures T_{g1}, T_{g2}), except for network VI, which contained only 3% w/w of PVTCA. *Figure 1* illustrates some typical results, as well as those with network VI. Under our conditions, therefore, all the networks, with the possible exception of VI, exist as two-phase systems.

Analysis of the slopes in volume/temperature diagrams such as *Figure 1* provides results of interest. We define S_1, S_3 as the slopes below T_{g1} and above T_{g2}, respectively, and S_2 as that in the intermediate region. If the coefficients of cubical expansion are additive we have:

$$S_1 = \alpha_{gpp}V_{gpp} + \alpha_{gpm}V_{gpm} + \alpha_{Hg}\Delta V_{Hg}$$

$$S_3 = \alpha_{1pp}V_{1pp} + \alpha_{1pm}V_{1pm} + \alpha_{Hg}\Delta V_{Hg}$$

(3)

in which the αs are the coefficients of cubical expansion and the Vs the volumes of the components at the appropriate temperature, and in the appropriate states, which are denoted by g (below glass transition) and 1 (above glass transition), respectively. Subscripts pp, pm refer to PVTCA and PMMA, respectively and ΔV_{Hg} is the difference between the volumes of mercury in the two dilatometers. Values of S_1 calculated from equations 3, with the aid of the measured coefficients of expansion, agree very closely with those observed. This is illustrated in *Figure 1*, in which lines with the calculated slopes are superimposed on the experimental points. In the temperature region just above T_{g2} the calculated values of S_3 also appear to be consistent with the experimental points, although there is some divergence above 115°C, especially with polymers relatively rich in PVTCA. This is attributable to thermal decomposition of the prepolymer, which has been shown in independent experiments to set in above 115°C.

Values of S_2 have been calculated from equation 4, analogous to 3, and are compared with the observed slopes in *Table 2*.

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$$S_2 = \alpha_{1pp}V_{1pp} + \alpha_{gpm}V_{gpm} + \alpha_{Hg}\Delta V_{Hg} \qquad (4)$$

It will be seen that for the PVTCA–PMMA networks the observed slopes are appreciably higher than those calculated (except for network VI). The assumption of independent behaviour of the two network components is therefore invalid in this region. We believe this implies that the two phases do not consist of the pure components, and that the phase relatively rich in PVTCA (phase 1) also contains PMMA *which partakes in the transition at* T_{g1}. We assume then that phase 1 contains all the PVTCA together with a fraction a of the PMMA in the network, while phase 2 consists of pure PMMA. This assumption leads to equation 5.

$$S_2 = \alpha_{1pp}V_{1pp} + a\alpha_{1pm}V_{1pm} + (1 - a) \; \alpha_{gpm}V_{gpm} + \alpha_{Hg}\Delta V_{Hg} \qquad (5)$$

Values of a may be calculated from equation 5 by equating S_2 with the observed slope and are shown in *Table 2*. The composition of phase 1 may readily be deduced from a and the overall composition of the network; we present in *Table 2* values of W, the weight of PMMA associated with unit weight of PVTCA in phase 1. It appears that this phase contains large proportions of PMMA, especially when the content of PMMA in the network is high. If phase 2 is not pure PMMA as assumed, but contains also some PVTCA which does not take part in the transition at T_{g1}, our calculations give underestimates of W.

The values of T_{g1} in networks I–V are perceptibly higher than T_{g1} for pure PVTCA (*Table 2*), and therefore support the view that phase 1 contains PMMA. On the other hand, T_{g2} is always close to the value for PMMA, as would be expected if phase 2 consists wholly of this polymer.

A blend of PVTCA and PMMA (52:48 w/w) behaves differently from the networks. It shows two transitions located at temperatures indistinguishable from the T_gs of the pure components, and the observed slope S_2 agrees with that calculated from equation 4 to within four per cent. Separation of the components is therefore much more nearly complete in this case.

The PVTCA–PSt networks VII–IX also show two glass transitions. As

Table 2. Network properties (PVTCA–PMMA, PVTCA–PSt systems)

Sample	$10^4 S_2$ (mlK^{-1}) obs.	calc.	a	W	PVTCA in network (% w/w)	T_{g1} °C	T_{g2} °C
I	3.75	2.64	0·326	1.2	21.5	74	97.5
II	5.23	4.66	0.15	1.7	8	71	102
III	3.83	3.57	0.071	2.1	3.5	69	101
IV	4.78	2.34	0.87	2.8	21	74	99
V	5.06	3.42	0.37	4.4	7.5	71	102
VI	3.41	3.51	—	—	3	—	103
VII	3.03	2.89	0.57	0.17	77	55	97
VIII	3.64	3.52	0.083	0.12	40.5	60	97
IX	4.00	3.85	0.061	0.22	21.5	60	100
PVTCA						59	
PSt							100
PMMA							103

with the other networks, the observed slopes S_1, S_3 agree with those calculated from equation 3 with the appropriate parameters for polystyrene (α_{gps}, V_{ps} etc.). Values of S_2 similarly estimated from equation 4 are again
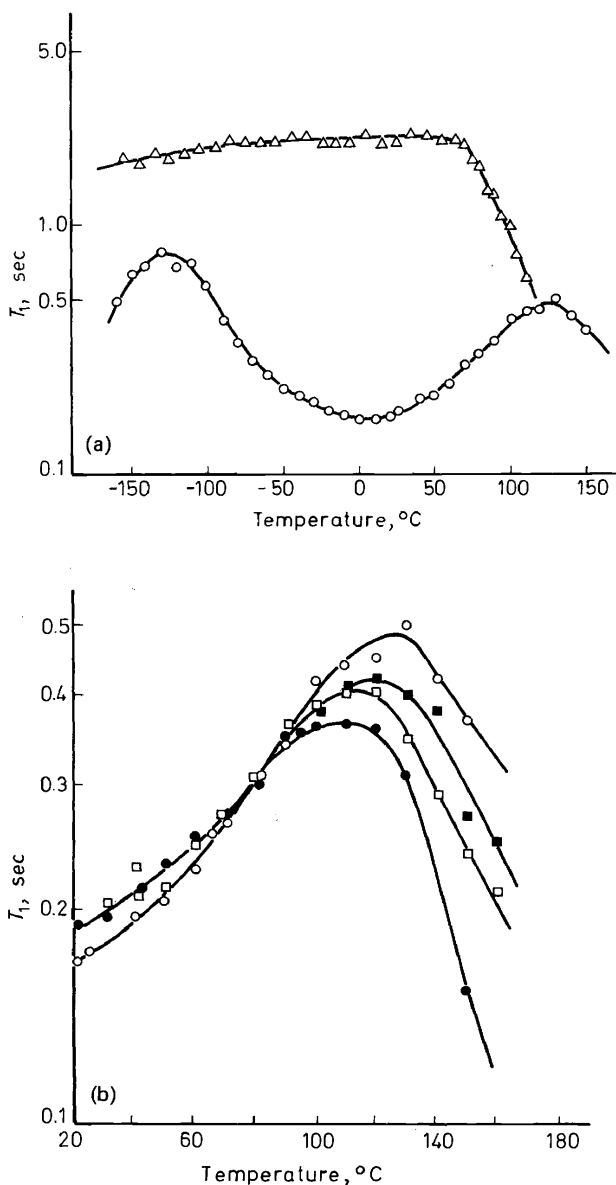

Figure 2. Dependence of spin–lattice relaxation time T_1 on temperature at 45 MHz. (a) $\triangle$ PVTCA homopolymer, $\bigcirc$ PMMA homopolymer; (b) $\bigcirc$ PMMA homopolymer, $\blacksquare$ PMMA/PVTCA network (88% w/w PMMA), $\square$ PMMA/PVTCA network (83% w/w PMMA), $\bullet$ PMMA/PVTCA network (50% w/w PMMA).

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higher than those observed (*Table 2*), but the differences are much smaller than with the PVTCA–PMMA networks. *Table 2* presents the derived values of α and W, which are also relatively low, showing that only small amounts of polystyrene are incorporated into phase 1. In agreement with this, we find that T_{g1}, T_{g2} for the networks are close to the transition temperatures of the pure components.

3.1.2 N.m.r. studies

Pulsed n.m.r. experiments on the PVTCA–PMMA system have been carried out to measure the relaxation times T_1 (spin–lattice) and T_2 (spin–spin). *Figures 2* (a, b) show the dependence of T_1 on temperature for PVTCA, PMMA and networks of PVTCA–PMMA. The rapid decrease in T_1 for PVTCA at temperatures exceeding 60°C, approximately (*Figure 2*a) is associated with the glass transition region, and demonstrates the sensitivity of the n.m.r. techniques to changes in molecular motion. At much higher temperatures, T_1 would be expected to pass through a minimum as the characteristic frequency of the motion passes through the experimental n.m.r. frequency (cf. Slichter[9]). A similar onset of chain motion occurs with the PMMA sample (*Figure 2*a) when the temperature reaches 100° to 110°C; in this case, however, the overall behaviour of T_1 is more complicated, and relaxation below this temperature region is mainly determined by a spin diffusion process through the rotating methyl groups.

Corresponding increases in T_2 for PVTCA and PMMA occur at 60°C and 110°C, respectively.

The variation of T_1 with temperature for the networks (*Figure 2*b) resembles that for pure PMMA, but the onset of mobility occurs at temperatures appreciably lower than that for MMA homopolymer. Since PVTCA protons make a negligible contribution to the n.m.r. signals, and hence to the measured T_1 in these networks, it follows that the decrease in T_1 arises from the onset of motion in the PMMA component. Thus the presence of PVTCA has induced motion in some PMMA chains at temperatures below the T_g of polymethyl methacrylate. Clearly this conclusion is in accord with dilatometric evidence indicating the existence of a composite phase 1 with a relatively low T_g. *Figure 2*b shows that the turning points in T_1 occur at successively higher temperatures in the network with increasing PMMA content. This also is consistent with the dilatometric results since, according to *Table 2*, the weight of PMMA in phase 1 of a given type of network (e.g. I, II, III) decreases with increasing PMMA content.

3.1.3 Mechanical properties

A few determinations are available of the glass transition temperatures derived from torsion pendulum measurements of mechanical loss tangents. The technique is not suitable for measuring both T_g values in these systems. Two PVTCA–PMMA networks and one PVTCA–PSt network were prepared, with structures summarized in *Table 3*. The glass-transition temperatures are shown in *Table 3*, together with values for the homopolymers and blends of the latter. T_g is higher for the PVTCA–PMMA networks than for the blend; the latter has a T_g identical with that of PVTCA. According to *Table 3*, the glass transition of the network containing 7% w/w PVTCA

Table 3. Properties of networks and blends (PVTCA–PMMA, PVTCA–PSt systems): glass transition temperatures from torsion pendulum observations

Sample	PVTCA in sample, % w/w	Mean no. of crosslinked units per weight-average PVTCA chain	$\bar{P}_n$ crosslinks	Branch: crosslink ratio	T_g °C
PVTCA	100	—	—	—	60 (0.35 Hz)
PMMA	0	—	—	—	105 (0.25 Hz)
PVTCA–PMMA network	7	11	2850	4	76 (0.54 Hz)
PVTCA–PMMA network	34	3	1690	4	73 (0.28 Hz)
PVTCA–PMMA blend	33	—	—	—	60 (0.20 Hz)
PVTCA–PSt network	25	8	1400	~0	60 (0.20 Hz)
PVTCA–PSt blend	26	—	—	—	60 (0.20 Hz)

is 16°C higher than the value for the blend. On the other hand, PVTCA–PSt networks and blends of the two homopolymers have similar values of T_g (60°C). These findings therefore reinforce the view that in our PVTCA–PMMA networks phase 1 contains PMMA in substantial amounts whereas in the PVTCA–PSt systems separation of the components is more nearly complete.

3.2 Networks containing polyvinyl bromacetate

Electron microscopy is capable of providing much direct information about the morphology of copolymers. Attainment of adequate contrast often necessitates use of a selective staining technique to create suitable variations of electron density in the specimen. Attachment of heavy atoms such as osmium and silver may be employed; thus most morphological studies of copolymers containing polydienes have involved the osmium tetroxide fixation treatment first used for these systems by Kato[10].

The networks we have considered so far do not respond to attempted staining by osmium tetroxide, since they do not contain suitable acceptor sites. Although it might be possible to introduce these by performing chemical reactions on the copolymers we feel that such treatments could alter the structures and introduce other complications. Preparation of a prepolymer containing bromine such as polyvinyl bromacetate therefore appeared to be of interest; the high reactivity of the bromine makes PVBA suitable for incorporation into networks by the technique described in § 2 and it seemed likely that domains of PVBA would be directly visible in the electron microscope by virtue of the high electron density associated with the bromine atoms.

In preliminary experiments carried out to investigate this aspect PVBA was crosslinked by PMMA; the gel time was 28 min, and specimens were prepared for examination after a reaction time of 10 min. These materials, which contained 60% w/w PMMA, therefore had a rather low crosslink
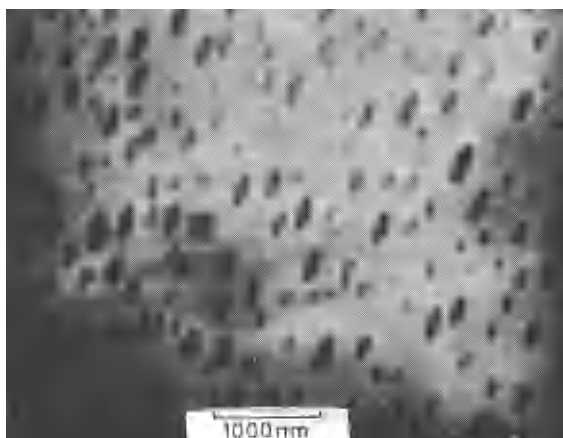
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Figure 3. Electron micrographs of film (thickness ~ 1 000 nm) of PVBA–PMMA network (60 % w/w PMMA) cast from MMA monomer.
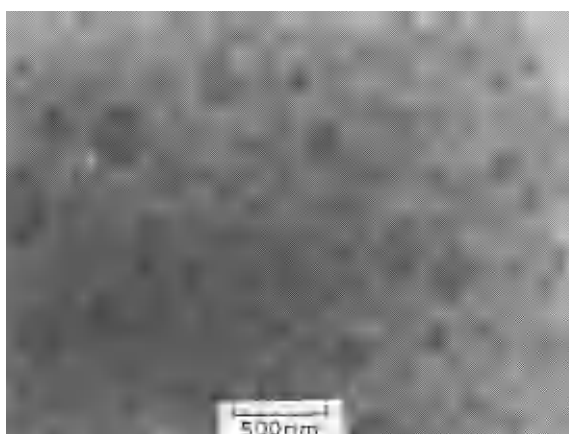

Figure 4. Electron micrograph of film (thickness ~ 1 000 nm) of PVBA–PMMA blend (76 % w/w PMMA) cast from MMA monomer.

density, one crosslinked unit being present in three weight-average **PVBA** chains, approximately. A high proportion of H-shaped molecules. and simple grafts of PMMA on to PVBA, would therefore be present.

Figures 3 and *4* show electron micrographs of films of the copolymer and a blend of the homopolymers cast from methyl methacrylate solution. *Figures 5* and *6* refer to specimens prepared by addition of PMMA and PVBA, respectively, to the crosslinked sample of *Figure 3* before casting. It is clear from these results that phase-separation in these systems can be observed directly in the electron microscope, without recourse to staining,
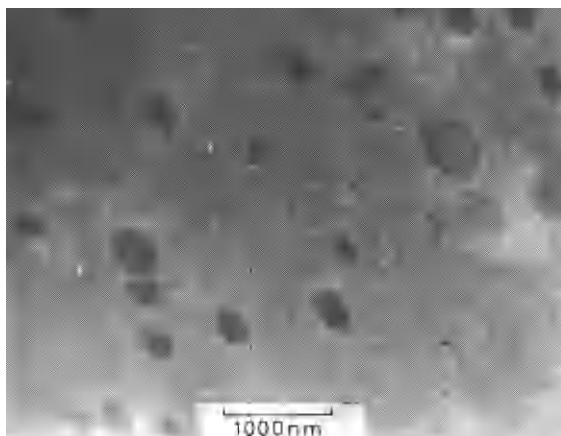
Figure 5. Electron micrograph of a film (thickness ~ 1 000 nm) of a blend of PVBA–PMMA network (60% w/w PMMA) and PMMA (44% w/w of whole specimen) cast from MMA monomer.
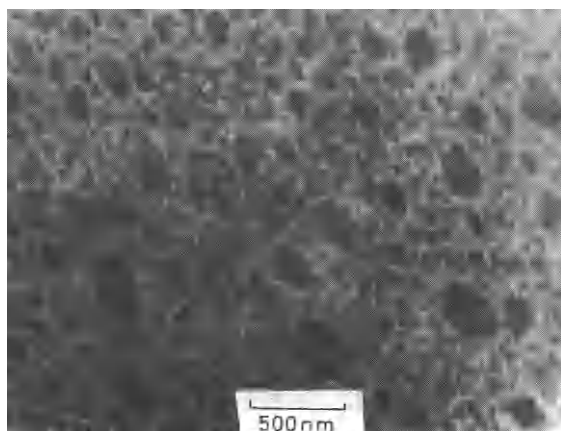

Figure 6. Electron micrograph of film (thickness ~ 1 000 nm) of blend of PVBA–PMMA network (60% w/w PMMA) and PVBA (44% w/w of whole specimen) cast from MMA monomer.

the PVBA component being, in effect, 'self-staining'. Further investigation of networks containing this polymer is in progress.

3.3 Networks containing chloroprene[11]

One of the main objectives in our programme of work on networks is the investigation of materials containing components with widely differing properties in the same network. Combination of hard and rubbery polymers

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is obviously an attractive possibility, particularly since such systems might provide information relevant to the fields of thermoplastic elastomers and impact-modified plastics. Neither butadiene nor isoprene is suitable for forming the rubbery segments, since these monomers polymerize only slowly in solution on account of high termination and low propagation velocity coefficients. Chloroprene (CP) appeared to be the most suitable monomer. Unfortunately, little quantitative information on the free-radical solution polymerization of chloroprene is available in the literature, and it was necessary to determine the kinetic parameter $k_p k_t^{-\frac{1}{2}}$ and the incidence of combination in the termination reaction. These data are necessary for derivation of the structural characteristics of the networks as described in § 2. This aspect of the work will only be summarized briefly here.

Polymerization of chloroprene (80% v/v in benzene) at 25°C was photo-initiated ($\lambda = 435.8$ nm) by manganese carbonyl in the presence of ethyl trichloracetate, rates of initiation being determined by comparable experiments with methyl methacrylate (compare § 2). The rate of polymerization was found to be directly proportional to the monomer concentration and the square root of the rate of initiation, showing that the reaction follows conventional free-radical polymerization kinetics. At 25°C, it was found that $k_p k_t^{-\frac{1}{2}} = 0.012 \pm 0.001 \text{ mol}^{-\frac{1}{2}} \text{ l}^{\frac{1}{2}} \text{ s}^{-\frac{1}{2}}$.

The nature of the termination reaction was investigated by the method devised by Bamford, Dyson and Eastmond[6], depending on determination of gel times in systems photoinitiated by PVTCA + $Mn_2(CO)_{10}$. It turns out that under our conditions termination occurs exclusively by radical combination. Networks prepared with chloroprene by our technique will therefore be substantially free from branches.

Two networks containing chloroprene were prepared with PVTCA as prepolymer. Some preparative details and structural parameters are given in
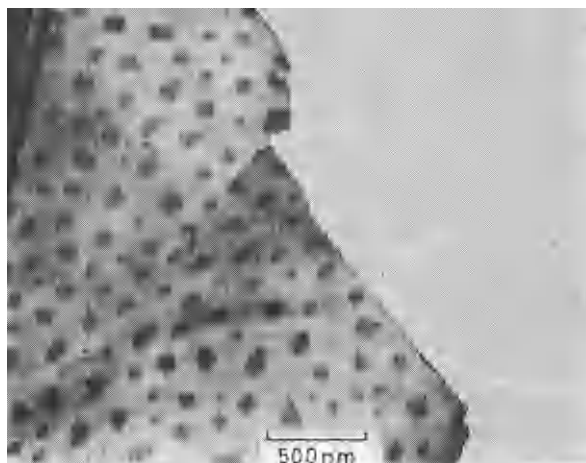

Figure 7. Electron micrograph of film (thickness ~ 100 nm) of PCP–PVTCA network I (Table 4) stained by osmium tetroxide.

Table 4. Figure 7 is an electron micrograph of a thin film of network I (*Table 4*) stained by exposure to osmium tetroxide vapour, and shows a relatively regular distribution of polychloroprene domains. The film thickness is probably of the order of the domain size and less than the average inter-domain separation, so that *Figure 7* is likely to represent a single layer of domains. *Figure 8* is an electron micrograph of a thin section of network II
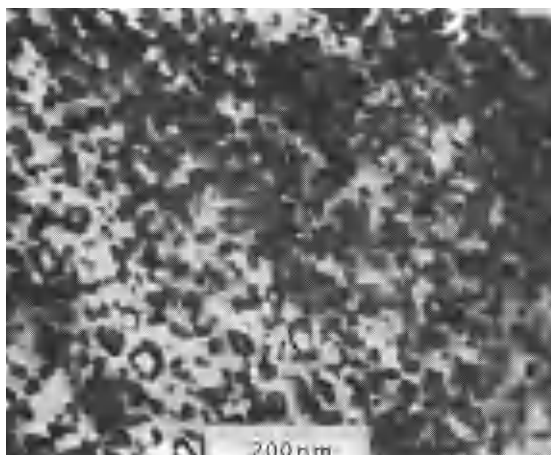

Figure 8. Electron micrograph of a section (thickness $\sim$ 80 nm) of PCP–PVTCA network II (*Table 4*) stained by osmium tetroxide.

(*Table 4*) cut from a specimen previously stained in aqueous osmium tetroxide. The distribution of domains appears less regular than that in *Figure 7*, but this may, in fact, be the result of damage during sectioning.

The mean interdomain separation in *Figure 7*, 200 nm, approximately, is greater than even the fully-extended length of an average PVTCA chain. It follows that the PCP domains cannot be connected by single PVTCA

Table 4. Network preparation and structure (PVTCA–PCP system)

Polymerization	I	II
Initial $[Mn_2(CO)_{10}]$, (mol l^{-1})	5.14×10^{-4}	6.4×10^{-4}
[PVTCA] (gl^{-1})	10	12.5
[M] (mol l^{-1})	8.16	7.65
Observed gel time (min)	44	3–4
Reaction time (min)	25	35
$10^9 I_0$ (mol l^{-1} s^{-1})	7.5	110
10^2 [ΔM] (mol l^{-1})	1.29 (calc.)	43
% chloroprene in network (w/w)	10.4	75.5
Mean no. of crosslinked units per weight-average prepolymer chain	0.57	11.7–8.8
$\bar{P}_n$ crosslinks	2290	3720

Polymerization temperature: 25°C. Diluent–benzene.

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molecules. The crosslink density in this polymer is low (*Table 4*) and the material must contain much unreacted PVTCA. Indeed, it is easy to show from the data in *Table 3* that the probability of a given PVTCA unit reacting during the network preparation is only 2×10^{-4}, approximately; consequently the majority of the copolymer molecules are H-shaped, with only minor amounts of more complex structures. We propose that the domains are formed by agglomeration of the PCP crosslinks of the polymer, with exclusion of most of the attached PVTCA, which therefore assumes the form of external branches and loops. The result is a PCP particle with attached PVTCA chains which confer stability when the particle is dispersed in a PVTCA matrix (consisting mainly of the unreacted polymer). From *Figure 7* we see that the average domain diameter is of the order 150 nm. This is similar in magnitude to the unperturbed mean end-to-end distance for a polychloroprene molecule with $\bar{P}_n = 2290$, so that most molecules could have their terminal groups on the surface of a domain, in agreement with our proposed model. A schematic drawing of the morphology is presented in *Figure 9*a.
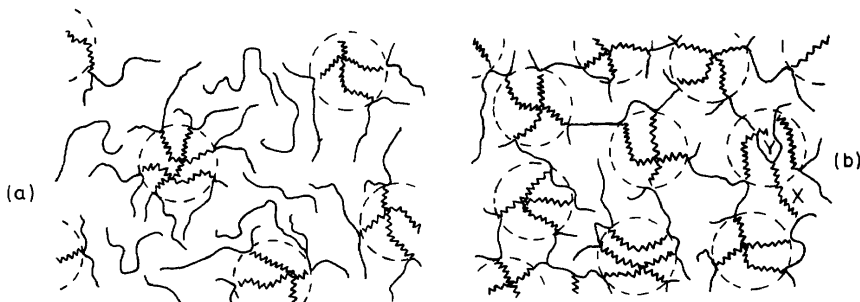

Figure 9. (a) Schematic representation of network I (*Table 4*). (b) Schematic representation of network II (*Table 4*. X, Y represent PCP, PVTCA chains trapped in the 'wrong' phases). ⌇⌇⌇⌇ PCP chains; ——— PVTCA chains.

The situation is naturally more complicated with network II (*Table 4*), in which the crosslink density is much higher. *Figure 8* suggests that the domain size is not very different (perhaps a little smaller), but the inter-domain separation is greatly reduced. We believe that the basic domain structure is similar to that in *Figure 9*a, but that the domains must now be linked together, predominantly by PVTCA (see *Figure 9*b), but probably by some polychloroprene in addition (X, *Figure 9*b). Geometrical constraints may necessitate the trapping of some PVTCA in PCP domains (Y, *Figure 9b*).

If these views are correct, it follows that the domain size in these systems should be mainly determined by the mean crosslink length, while the inter-domain separation should depend on the density of crosslinking.

Figure 10 shows the structure of a film cast from a blend of the homo-polymers; it resembles electron micrographs of many blends of incompatible polymers[12]. Comparison of *Figures 7, 8* and *10* shows that only in the blend are large PCP domains (~ 2000 nm) in evidence. Growth of a domain in
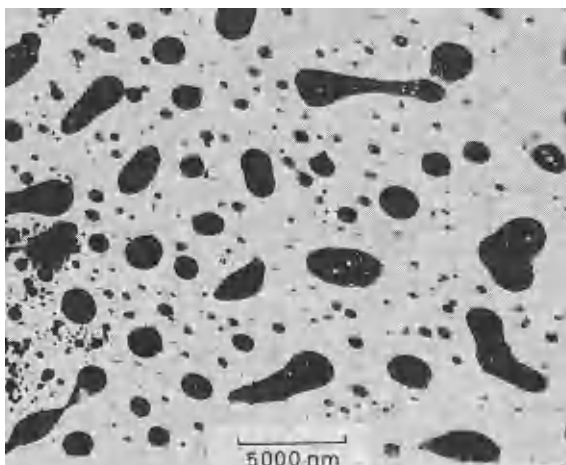
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Figure 10. Electron micrograph of film (thickness 2 000 nm) of blend of PVTCA and PCP (14 % w/w) stained by osmium tetroxide.

the crosslinked polymer beyond the stage represented in *Figure 9*a would require further incorporation of PVTCA, and would therefore be thermodynamically unfavourable.

4. GENERAL

The evidence we have presented suggests that the existence of two phases in networks of the type described is of common occurrence. The factors which influence the morphology of these materials are naturally more complex than those operative in simple block copolymer systems. In the networks, natural incompatibility of polymers is opposed by geometrical constraints which prevent complete separation of the components in the absence of chain rupture. The opposition gives rise to the formation of phases containing both components intimately dispersed, which, at least in some systems (e.g. PVTCA–PMMA) behave like a pure component and exhibit a single glass transition. Such phases are less commonly encountered with mixtures of homopolymers and their appearance in networks may be attributed to 'enforced compatibility'. Their composition would be expected to be determined *inter alia* by the degree of incompatibility of the homopolymers, the density of crosslinking and the overall composition of the system. Thus we believe that PVTCA and PMMA are less incompatible than PVTCA and PSt, and that this is one factor accounting for the differences in behaviour of the networks. The importance of differences in crosslink length and the presence of branches is not yet clear, and further work in this area is required.

The behaviour of the systems containing chloroprene indicates the way in which morphology may be influenced by the density of crosslinking, and we hope that further studies will reveal and elucidate a corresponding influence on mechanical properties.

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