New polyisobutylene-based UV-curable flexible coatings

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SUMMARY

New UV-curable solventless flexible transparent coatings
have been prepared of acrylate- and methacrylate-capped linear
or three-arm star polyisobutylenes PIB in the presence of con-
ventional "reactive diluents" (multifunctional acrylate or
methacrylate esters) and a UV-sensitizer. Solvent extraction
studies show essentially complete network formation. The swell-
ing ratios were surprisingly small indicating highly cross-
linked gels. Films cast on glass, Teflon, stainless steel and
aluminum and UV cured very strongly adhere to these surfaces
and could not be removed without destroying the films. Films
obtained by casting on aluminum, UV curing and subsequently
dissolving the support by concentrated NaOH, contain no pin-
holes. DSC traces show a low and a high temperature transition
characteristic of a domain separated morphology of soft PIB and
hard acrylate or methacrylate segments. The exact positions of
the transitions in the range from -57 to -45°C, and from 62 to
78°C are affected by the overall film composition. Tensile and
elongation data have been obtained. The water absorption of
these highly hydrophobic coatings is negligible.

INTRODUCTION

High energy radiation curable coatings are of great current
interest particularly for the electronics industry (1-3). UV
curable compositions usually contain a base polymer (e.g., a
polyester or polyether carrying acrylate A or methacrylate MA
functions) and one or a combination of various low molecular
weight A or MA esters to dilute the base polymer. The latters
are termed "reactive diluents" because they incorporate into
the final network (4-6). Thus the processing characteristics
and properties of UV-cured coatings reflect those of the indi-
vidual components. For example, flexibility may be improved by
the use of reactive diluents with long hydrocarbon or polyether
chains (i.e., $MA-(CH_2)_6-MA$, $MA-(CH_2CH_2O)_n-MA$), crosslink den-
sity may be increased by multifunctional reactive diluents, etc.
Efforts have been made to modify the properties of UV-curable
coatings by the incorporation of polar rubbers, i.e., fluoro-
carbon rubbers (7), nitrile rubbers (8). Nonpolar PIB-based
rubbers have not yet been used in UV-curable formulations, most
likely because of lack of suitably functionalized PIB

derivatives capable of being incorporated into an acrylate net-
work. The incorporation of PIB into UV-curable coatings would
be of interest on account of the desirable combination of pro-
perties this rubber represents, e.g., outstanding chemical,
weathering, and moisture resistance, barrier properties.

It has been demonstrated in these laboratories that neat
MA-PIB-MA under UV-radiation yields crosslinked networks, how-
ever, 20% extractables remain, most likely on account of
reduced mobility of the MA-capped polymers with progressing
crosslinking (9). It was of interest to continue this research
with A- and MA-capped PIB base polymers in conjunction with
select reactive diluents that impart mobility and thus would
facilitate complete crosslinking of the highly viscous charge.
Thus we employed as reactive diluents the commercially avail-
able 2-ethyl-2-(hydroxymethyl)-1,3-propanediol triacrylate and
2-ethyl-2-(hydroxymethyl)-1-,3-propanediol trimethacrylate
(trimethvlolpropane-triacrylate and -trimethacrylate, TMP-TA
and TMP-TMA).

This paper concerns the synthesis of largely solventless
UV-curable flexible coatings from A-PIB-A, MA-PIB-MA and
MA-PIB-MA base polymers in combination with the above two con-
  |
  MA
ventional reactive diluents, and a preliminary characterization
of the flexible films obtained.

EXPERIMENTAL

A. Materials

The synthesis and purification of linear dihydroxyl tele-
chelic PIB (HO-PIB-OH) (10) and triarm-star trihydroxyl tele-
chelic HO-PIB-OH (11) have been described. 1,3,5,-Tri-
      |
      OH
phenyl verdazyl (TPV) was synthesized from 1,3,5-triphenyl
formazan (12). Acryloyl chloride and methacryloyl chloride
were distilled before use. Methylene chloride, chloroform,
n-hexane, n-pentane, benzene and carbon tetrachloride were
dried over molecular sieves (3Å). TMP-TA, TMP-TMA (Aldrich,
pale yellow liquids), 2,2-dimethoxy-2-phenyl-acetophenone
(Irgacure 651, Aldrich)), and NaOH were used as received.

B. Procedures

Synthesis of A-PIB-A, MA-PIB-MA and MA-PIB-MA
                                  |
                                  MA

To 10 g of telechelic PIB-diol (HO-PIB-OH, $\overline{M}_n$=17,000) dis-
solved in a mixture of 180 mL methylene chloride and 20 mL
chloroform were added 15 mL triethylamine. Then 5 mL freshly
distilled acryloyl chloride were added dropwise to the charge
at 0°C under a nitrogen atmosphere and the mixture was stirred
overnight at room temperature. A few drops of TPV solution
were added to prevent crosslinking and the solvents, triethyl-
amine, and acryloyl chloride were removed by a rotary evapo-
rator. The polymer was dissolved in a methylene chloride/
n-hexane mixture (40/60 v/v), washed several times with 1%
acetic acid to remove traces of triethylamine, neutralized
with aqueous sodium bicarbonate, and washed with distilled

water. The solution was dried over $CaCl_2$ overnight and after adding a few drops of TPV solution the solvents were evaporated. Polymer functionality was $\overline{F}_n$=2, determined by FTIR spectroscopy. The analytical technique has been reported (13).
The syntheses of MA-PIB-MA (M_n=3000) and MA-PIB-MA ($\overline{M}_n$=
MA
3300) were similar to that described above, except that methacryloyl chloride was used for esterification and the polymers were washed in pure methylene chloride solution. Product functionalities were $\overline{F}_n$=2 and 3, respectively, as determined by FTIR spectroscopy (13).

C. Characterization Methods

Molecular weights were determined by a Waters Associates high pressure GPC instrument (Model 6000A pump, WISP 710B automatic injector, a series of five µ-Styragel columns (10^5, 10^4, 10^3, 500 and 100 Å), Differential Refractometer 2401, and UV Absorbance Detector 440). A calibration curve was made with well-fractionated PIB standards. The flow rate of THF was 1 mL/min.

UV-curing: Solutions in CCl_4 used to prepare films for UV-curing (Table I) were poured into thin Al weighing dishes and the solvent was evaporated by first storing the films in a hood at room temperature followed by drying in a convection oven under nitrogen at 55°C. The films were irradiated for 10-30 seconds with a Portacure F1500 UV-curing unit (American Ultraviolet Co.) under a blanket of nitrogen. After dissolving the Al base by conc. aqueous NaOH the resulting films (0.02-0.03 cm thick) were washed with distilled water to remove the surface debris (Al_2O_3, etc.) and dried in a vacuum oven at 55°C for 24 hours.

Swelling and extraction experiments were carried out with n-pentane or benzene using samples (about 2x2x0.02 cm) cut of the films. The thickness of the films (usually 0.01-0.03 cm) was measured by a thickness gauge. Density of the films was calculated from size and weight data. Equilibrium swelling have been reached after a few days. Results in Table II are averages of at least three measurements. Water absorption was determined by ASTM-D570. Preweighed samples (about 2x2x0.02 cm) were immersed in distilled water at 75°C for 48 hours and the weight gain (percentage) was calculated. Values in Table IV are averages of at least three measurements. DSC analyses were carried out on a DuPont 1090 Thermal Analyzer at 20°C/min heating rate. The position of the Tg's were determined by the midpoint method. Stress-strain data were obtained on an Instron Universal Testing Instrument with a 500 g load cell and 10 cm/min crosshead speed at room temperature using microdumbbells.

RESULTS AND DISCUSSION

Table I summarizes some characteristics of the functional PIB base polymers and the composition of the UV-curable formulations.

TABLE I

Systems Used to Prepare Films for UV Curing Experiments*

Network Symbol	Polymer Symbol	g	$\overline{M}_n$	Reactive diluent(% on base polym.)	CCl₄ mL	Visual Observa- tions
DA-10	A-PIB-A	5	17,000	10-TMP-TA	5	clear film
DA-20	A-PIB-A	5	17,000	20-TMP-TA	5	heterogeneous film
DMA-10	MA-PIB-MA	5	3,000	10-TMP-TMA	-	light yellow, transparent film
DMA-20	MA-PIB-MA	5	3,000	20-TMP-TMA	-	light yellow, slightly opaque film
TMA-10	MA-PIB-MA MA	5	3,300	10-TMP-TMA	-	light yellow, transparent film

*One mL of a 20% Irgacure 651 in CCl₄ solution was added to each composition.

The network symbol indicates the type of functional PIB base polymer and the amount of reactive diluent in wt% (rela- tive to the polymer). For example, DA-10 stands for a network prepared with a linear diacrylate DA and 10% reactive diluent. The films were UV-irradiated as described in Experimental. Irgacure 651 is an efficient photoinitiator that produces reactive CH₃· radicals which induce the polymerization of acry- late- or methacrylate groups (1). Irradiation yielded color- less (DA-10) and light yellow (DMA-10, DMA-20 and TMA-30) flexible films. Films prepared with the relatively high mole- cular weight diacrylate and 20% TMP-TA exhibited phase separa- tion (light yellow acrylate islands in the colorless base polymer matrix) and have not been further characterized. The DMA-10, DMA-20 and TMA-10 networks are essentially solventless and only the addition of photoinitiator introduced a minimum amount of CCl₄. DMA-20 did not show phase separation in spite of the high concentration (20%) of the reactive diluent used. In DMA-20 the molecular weight of the MA-PIB-MA is much lower ($\overline{M}_n$=3000) than that of the A-PIB-A in DA-20 ($\overline{M}_n$=17,000) so that the MA-group concentration is much higher in the former than the A-group concentration in the latter.

Difficulties were encountered on trying to remove the films from the various casting surfaces. The use of silicon-type releasing agent did not help (because the compositions did not wet the surface). Attempts to remove films from glass or stainless steel or even Teflon surfaces by the use of knives wetted by nonsolvent (e.g., MeOH), a method that has often been used in similar situations, was found to be completely inade- quate with the present networks. Satisfactory films for

further testing could only be obtained by casting on aluminum and dissolving the support by conc. NaOH solution. This method also gave information about possible pinholes and imperfections in the films. Pinholes can be readily detected visually as black spots if the conc. NaOH solution penetrates through the pinholes and destroys the shiny Al surface. In our experiments in the conc. NaOH solution was unable to penetrate thin films and pinholes (black spots) could not be detected. Dissolution of the Al proceeded exclusively from the uncovered parts (bottom and sides). A film (DMA-10) has been exposed to conc. (98%) H_2SO_4 for 24 hrs at room temperature. While strong discoloration (to brown) occurred, the film remained flexible. These tests demonstrate the outstanding caustic and acid resistance, and very strong adhesion of the films. Films were characterized by extraction, swelling, DSC, water absorption and stress-strain studies.

Extraction with n-pentane or benzene showed the sol fraction to be consistently negligible (<5%). Low extractables indicate essentially complete crosslinking (14).

Attempts were made to calculate $\overline{M}_c$ (the molecular weight of sequences between crosslinking points) by the Flory-Rehner equation (15) where ν is the number of effective chains per

$$\nu = \frac{-[\ln (1-V_r) + V_r \chi V_r^2]}{V_o(V_r^{1/3} - 2V_r/f)} = \frac{\delta}{M_c} \tag{1}$$

volume of network, V_r is the volume fraction of network in the swollen system, V_o is the molar volume of the solvent, χ is the polymer-solvent interaction parameter, δ is the density of the unswollen network, and f denotes the crosslink-functionality (the number of chains emanating from each crosslink). The density of the films was found to be essentially equal to the density of PIB (δ =0.92 g/cm) (16). f was assumed to be large so

$$V_r^{1/3} - 2V_r/f = V_r^{1/3} \tag{2}$$

and the χ values given the PIB-n-pentane (0.49) and PIB-benzene (0.50) systems were used for the calculations (15). Experimental results are shown in Table II.

$\overline{M}_c$ values obtained by the use of both n-pentane and benzene are similar; however, they are much lower than the theoretical values expected for perfect networks from the $\overline{M}_n$ data shown in Table I. Irradiation of MA-PIB-MA in the absence of reactive diluents also gave surprisingly low $\overline{M}_c$ values by swelling in benzene (9). It is difficult to account for these data, however, some cautious generalizations can be made: First, the Flory-Rehner equation (1) developed for measuring the crosslink density of defect-free cured homogeneous (one component) rubbers, may not be valid for heterogeneous (two component) networks with many defects (i.e., dangling ends, entanglements). Second, χ values are unavailable for two

TABLE II

Swelling of Networks in n-Pentane and Benzene at
Room Temperature

Network Symbol	V_r	n-Pentane ν L/mole	$\overline{M}_c$	V_r	Benzene ν L/mole	$\overline{M}_c$
DA-10	0.347	2.49×10^{-4}	3700	0.342	2.8×10^{-4}	3200
DMA-10	0.701	2.59×10^{-3}	350	0.623	2.05×10^{-3}	450
DMA-20	0.711	2.74×10^{-3}	340	0.656	2.52×10^{-3}	370
TMA-10	0.745	3.35×10^{-3}	280	0.664	2.64×10^{-3}	350

component networks and no guidelines exist how this parameter should be chosen for such systems. We have determined $\overline{M}_c$ values by the use of two solvents, n-pentane that is a good solvent for PIB but is a nonsolvent for the A or MA moiety, and benzene that is a bad solvent for PIB but a good solvent for the A or MA systems; however, we obtained very similar swelling data with both solvents. Similar observations have been reported for PIB-based urethane networks (11). In view of this the ν values in Table II are difficult to interpret and would require theoretical foundation. The data nonetheless indicate that the networks are highly crosslinked.

The microarchitecture of the films has been studied by DSC. Figure 1 and Table III show the results. Two transitions are present, a Tg in the range from -57 to -45°C and another from 62 to 78°C.
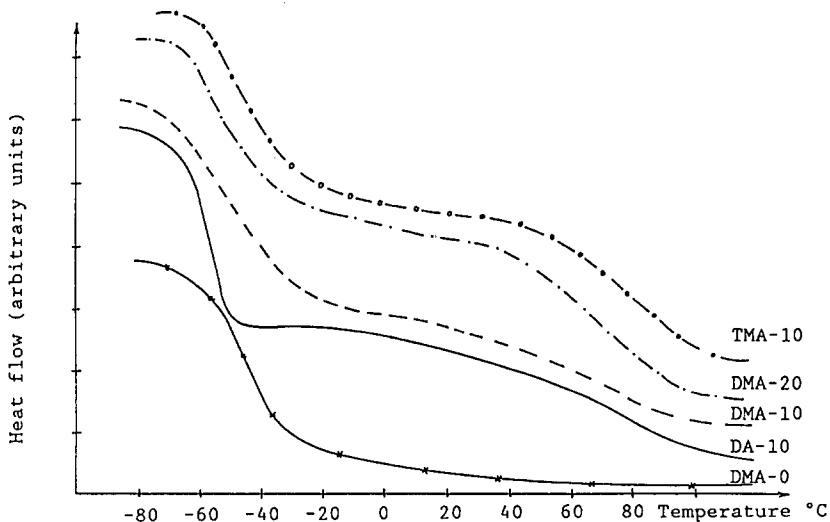

Figure 1. DSC traces of UV-cured films

TABLE III

Tg Values of UV-Cured Networks

Network Symbol	T_g	
DMA-0	-47	-
DA-10	-57	+60 (very weak)
DMA-10	-52	+62
DMA-20	-50	+72
TMA-10	-45	+78

The DSC traces of DMA-0 (i.e., a MA-PIB-MA of $\overline{M}_n$=3000, UV crosslinked in the absence of reactive diluent but otherwise under the same conditions as the other films) show only the low temperature Tg characteristic of PIB. The high temperature Tg's characteristic of the polyacrylate or methacrylate domains are less distinct on account of the relatively low amounts (10-20%) of these ingredients in the films. The exact positions of the Tg's are affected by the composition of the films: higher crosslink density (decreased mobility of the PIB chains) increases the low temperature Tg and higher active diluent concentration gives higher high temperature Tg values.

The stress-strain properties of the films have been investigated. Table IV shows tensile and elongation data. By increasing the hard phase content, tensiles increase while elongations decrease. The three-arm star base polymer shows the lowest values conceivably due to its high crosslink density.

The water absorption of the networks has been determined. According to the data shown in Table IV water absorption is negligible which is in line with the highly hydrophobic nature of the PIB base polymer.

TABLE IV

Tensile Properties and Water Absorption of UV-Cured Networks

Network Symbol	σ kg/cm^2	ε %	Water Absorption %
DA-10	4.0	125	0.0
DMA-10	8.3	120	5.0
DMA-20	25.0	50	0.0
TMA-10	5.4	80	5.0

CONCLUSIONS

On the basis of these investigations these crosslinked films are proposed to comprise a soft continuous PIB matrix (80-90%) embedded into which are hard PA or PMA domains (10-20%). The hard domains are widely dispersed in the soft matrix and their average size must be well below the wavelength of visible light since the films are transparent (except for the DMA-20 which if slightly opaque on account of the relatively

higher concentration of TMP-TMA used. Similarly to our earlier model (9), Figure 2 helps to visualize the secondary micro- structure. The films exhibit a desirable combination of pro- perties of the base polymer and the reactive diluent which is of promise for electronic, biomedical, specialty coating, adhesive, sealant, etc., applications
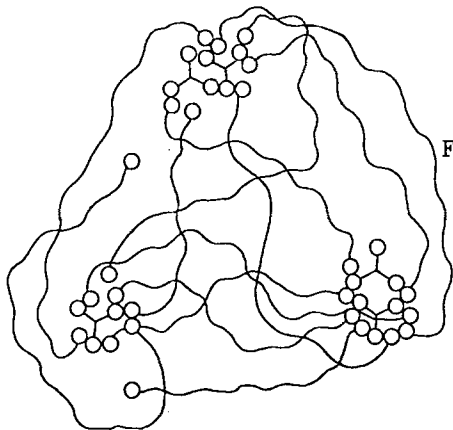

Figure 2.   Idealized structure of network prepared from MA-PIB-MA and 20% TMP-TMA where $\sim\!\!\sim$ = PIB, o = MA groups and = TMP-TMA.

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