



International Conference

Toughening of Plastics

4—6 July 1978

**The Regent Centre Hotel
Carburton Street
London W1P 8EE**

**THE PLASTICS AND RUBBER INSTITUTE
11 HOBART PLACE · LONDON SW1W 0HL**

TOUGHENING OF PLASTICS

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INFORMATION

conference

One of the main objectives of the conference is to take stock of current knowledge relating to the industry, including the chemistry of toughening, manufacture of toughened polymers, structure property relationships, rheology, melt processing and extrusion, and the economic outlook for toughened plastics.

For

The conference is being sponsored by the Polymer Properties Group of the Institute of Plastics and Rubber Institute.

The organizing subcommittee comprises:

Chairman:	C B Bucknall	Cranfield Institute of Technology
Members:	M B Hopkins A J Kinloch J G Williams J Young	Dow Chemical Co Ltd Ministry of Defence Imperial College of Science and Technology Borg-Warner Chemicals
Secretary:	C A Alcorn (Mrs)	The Plastics and Rubber Institute

Due

A conference will be held at the Regent Centre Hotel, Carburton Street, London W1P 3EE. The hotel is within walking distance of the following underground stations:

Regents Park
Great Portland Street
Warren Street

A map is included on page vi for your guidance.

The telephone number of the Regent Centre Hotel is: 01-388 2300.

reprints

This booklet contains the texts of papers as submitted by the authors in the form of camera-ready copy. Papers have not been edited by the Institute staff.

Publication of the proceedings

It is hoped to prepare a general report on the conference to be considered for publication in a future issue of the Institute's members' journal 'Plastics and Rubber International', together with selected papers. The copyright of the papers is claimed initially by the Plastics and Rubber Institute.

Programme and timetable

This is detailed on pages iii to v.

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Accommodation

Delegates are responsible for arranging their own accommodation. However, an allocation of rooms is available at the Regent Centre Hotel, London. Any delegate wishing to reserve accommodation should do so as soon as possible by contacting the Regent Centre Hotel, Carburton Street, London 8EE (telephone 01-388 2300 - Telex 22453) asking for an allotment to be put out of the PRI's conference reservation.

VAT invoice

All those who have requested a VAT invoice (and paid the appropriate fee) will find the invoice enclosed. Please pass it to your accounts department.

Name Badge and list of delegates

The list of delegates and name badges will be available for collection at the conference office. Delegates are requested to wear their name badges throughout the event. Authors, chairmen and committee members will wear RED name badges.

Conference Dinner

All delegates who have registered for the duration of the conference have paid for their conference dinner. Additional dinner tickets may be available and application should be made to the Plastics and Rubber Institute prior to the meeting or at the conference reception desk during the meeting.

Discussions

The discussion periods will be an important part of the meeting and the cooperation of all concerned is sought in ensuring that the timetable is adhered to. When the time for discussion becomes short, delegates are asked to keep their contributions concise to allow the maximum number to participate.

Reception desk

Institute staff will man an enquiry/reception desk where delegates may ask messages or seek information. However, delegates can only be contacted during convenient breaks in the programme.

A selection of the Institute's publications will be available for perusal or purchase.

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PROGRAMME

Tuesday 4 July 1978

Chairman: DR C B BUCKNALL (Cranfield Institute of Technology)

Arrival - registration and coffee

- 1 Phase separation in rubber-polystyrene systems
H KESKKULA (The Dow Chemical Co, USA)

Discussion

- 2 Simulating and interpreting the HIPS process
DR G F FREEGUARD (University of Nottingham)

Discussion

- 3 Some new approaches to rubber-modified polymers
PROF G RIESS (Ecole Nationale Supérieure, France)

- 5 Discussion

Lunch

Chairman: PROF G ALLEN (Science Research Council)

- 4 Economic survey of rubber-toughened plastics 1973-83
J S MURPHY (Plastics Industry Europe)

Discussion

- 5 Stabilization of rubber modified plastics against environmental degradation
PROF G SCOTT (University of Aston)

Discussion

- 6 Investigation of the structure of copolymers by means of carbon-13 NMR spectroscopy
A D H CLAGUE and J P C M VAN DONGEN (Shell, Amsterdam)

Discussion

Tea

- 7 Modification of styrene-acrylonitrile copolymers, vinyl chloride polymers and cellulose esters by EVA co-polymers

Discussion

- 8 Inferences on polypropylene/EPDM blend toughness from morphology and component rheology
S MILLER (General Electric Co, USA)

Discussion

Close

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PROGRAMME

Wednesday 5 July 1978

Chairman: W J FRAZER (Borg-Warner Chemicals, Amsterdam)

0900 9 Rheological properties of molten high-impact polystyrene and ABS polymers in comparison with polystyrene
DR H MUNSTEDT (BASF, Germany)

0925 Discussion

0930 10 ABS resins: the relationship between rheological behaviour and the gloss of plastic items
A MORONI and A CASALE (Montedison, Italy)

0955 Discussion

1000 Open Forum

1030 Coffee

1100 12 The effect of molecular orientation on the mechanical properties of rubber-modified polystyrene - results obtained by IUPAC working party
DR W RETTING (BASF, Germany)

1155 Discussion

1200 13 ✓ Stress whitening of rubber modified thermoplastics
DR H BREUER, DR J STABENOW and DR F HAFF (BASF, Germany)

1225 Discussion

1230 Lunch

Chairman: PROF G WILLIAMS (Imperial College of Science and Technology)

1400 14 Impact behaviour of nylon-66 compositions: ductile-brittle transitions
DR E A FLEXMAN (DuPont, USA)

1425 Discussion

1430 15 A toughened mechanism in particulate rubber/epoxy composites
MISS S C KUNZ, DR P W R BEAUMONT and PROF M F ASHBY (University of Cambridge)

1455 Discussion

1500 Open Forum

1530 Tea

1600 16 Crazing in block copolymers
PROF A S ARGON, PROF R E COHEN BZ JANG and PROF J VANDER SANDE (Massachusetts Institute of Technology)

1625 Discussion

1630 17 Impact toughness and heat generation at crack tip in ABS
S K GAGGAR and JR WILSON (Borg-Warner, USA)

1655 Discussion

1700 Close

1730 Conference Dinner

Paper 11 was withdrawn

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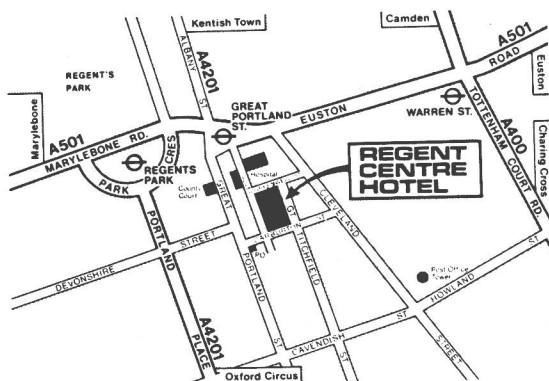
PROGRAMME

Thursday 6 July 1978

Chairman: PROF A S ARGON (Massachusetts Institute of Technology, USA)

- 0900 18✓ The impact behaviour of ABS over a range of temperatures
MRS L V NEWMANN and PROF J G WILLIAMS (Imperial College of
Science and Technology)
- 0925 Discussion
- 0930 19 Effects of temperature and strain rate on JIC and KIC of ABS
POLYMERS
PROF L J BROUTMAN and DR N S SRIDHARAN (Illinois Institute of
Technology, USA)
- 0955 Discussion
- 1000 20✓ Fracture toughness studies on rubber-toughened polymers
A F YEE and R P KAMBOUR (General Electric Co, USA)
- 1025 Discussion
- 1030 Coffee
- 1100 21 The impact strength of HIPS and the role of rubber content
K NIKPUR and PROF J G WILLIAMS (Imperial College of Science and
Technology)
- 1125 Discussion
- 1130 22 Adhesive fracture behaviour of CTBN-modified epoxy polymers
W D BASCOM and D L HUNSTON (Naval Research Laboratory, USA)
- 1155 Discussion
- 1200 23 Developments in improved crack resistance of thermoset resins and
composites
E H ROWE (B F Goodrich Co, USA)
- 1225 Discussion
- 1230 Lunch
- Chairman: PROF L J BROUTMAN (Illinois Institute of Technology, USA)
- 1400 24 Fatigue of ABS: deformation and failure under tension-
compression cycling
DR C B BUCKNALL and W W STEVENS (Cranfield Institute of
Technology)
- 1425 Discussion
- 1430 25 Fatigue crack propagation response of toughened engineering
plastics
M D SKIBO, J JANISZEWSKI, R W HERTZBERG and J A MANSON (Lehigh
University, USA)
- 1455 Discussion
- 1500 26 Influence of viscosity on the GIC-C relationship for rubber
modified plastics in environmental stress cracking liquids
R P KAMBOUR and A F YEE (General Electric Co, USA)
- 1525 Discussion
- 1530 Close of conference
Tea

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THE PLASTICS AND RUBBER INSTITUTE

The Plastics and Rubber Institute - an amalgamation of the Institution of the Rubber Industry, founded in 1921, and the Plastics Institute, founded in 1931 - is a registered educational charity and the oldest and largest international professional society in the world which is devoted exclusively to providing a service for personnel employed in the plastics and rubber, and allied industries.

The Institute's principal aims and objectives are: the development for the public benefit of a professional body comprising members concerned with the art, science and technology of plastics, rubbers and other high polymers in academic, research, commercial and administrative capacities, and the advancement of the standard and methods of education and training at all levels in these fields and related technical and non-technical subjects, including management, economics and finance.

The present membership total some 12,000 individuals of whom about 5,000 are resident overseas. There are 16 geographical sections in the UK and 11 overseas - Australasia, Belgium, Hong Kong, India, Malaysia, Netherlands, Pakistan, Rhodesia, South Africa, Sri Lanka and General Overseas.

The Institute (a) organizes about 200 meetings each year from headquarters and in the local sections (b) publishes bi-monthly 'Plastics and Rubber International'; two quarterly research journals concerned with 'Materials and Applications' and 'Processing'; and a range of over 45 books, pamphlets and educational material (c) is a qualifying body and the grades of membership awarded are: Fellow (FPRI), Associate (APRI), Associate Member (AMPRI), Graduate (GradPRI), Technician (TPRI) and Licentiate (LPRI). APRI and AMPRI are degree equivalent qualifications.

Annual subscription

Student	UK	£5.00	General Overseas Section	£4.00
Ordinary (under 25)	UK	£7.00	General Overseas Section	£5.50
Ordinary	UK	£15.00	General Overseas Section	£11.00

CONTRIBUTORS' BIOGRAPHICAL NOTES

Prof A S Argon, BS, AM, ScD, is Professor of Mechanical Engineering at the Massachusetts Institute of Technology (MIT) in Cambridge, Mass, USA, where he has recently been Head of the Mechanics and Materials Division. His research is in the area of mechanisms of inelastic deformation and fracture of solids to which he has made extensive contributions. He has been Visiting Professor of Polymer Physics at the University of Leeds in the UK during 1971-1972.

Prof M F Ashby was Professor of Applied Physics at Harvard University between 1969-1973. He joined the University of Cambridge in 1973 as professor in the Department of Engineering.

Dr P W R Beaumont was assistant professor in the Department of Materials at the University of California, Los Angeles between 1970-1973. He joined the University of Cambridge in 1973 as lecturer in the Department of Engineering.

Dr H Breuer graduated with a degree in physics from Technische Hochschule Aachen in 1965. After postdoctoral work at the same university he joined the R & D Department for polymers of Wacker-Chemie in 1967 and transferred to BASF Aktiengesellschaft in 1969, where he did some research work on fibres and plastics.

Prof L J Broutman is Professor of Materials Engineering in the Department of Metallurgical and Materials Engineering and Director of the Mechanics and Materials Research Laboratory at IIT. Dr Broutman received BS, MS and an ScD degree in Materials Engineering and Science from MIT in 1963. From 1963 to 1966 he was a Senior Research Engineer at IIT Research Institute and in 1966 joined the faculty of the Department of Mechanics at IIT. Dr Broutman is co-editor of the book, *Modern Composite Materials*, published by the Addison-Wesley Co, co-editor of the recent 8 volume series "Composite Materials" for Academic Press, and author of 80 papers in the areas of mechanics of polymers and composite materials. Dr Broutman serves as a consultant to many private industrial companies as well as the Department of Housing and Urban Development. This year Dr Broutman has been elected President of the International Society of Plastics Engineers, Inc, at 19,000 member professional society.

Dr C B Bucknall graduated from the University of Cambridge with degrees in Natural Sciences. After a period of National Service, he joined the Research Department of BXL at Manningtree, Essex, where he worked for eight years on mechanical properties of plastics. In 1967 he moved to Cranfield Institute of Technology, where he is now Senior Lecturer in the Department of Materials.

Dr A D H Clague received his Bachelor's degree in chemistry from the Manchester College of Science and Technology in 1961, and his Master's degree (1963) and PhD (1966) in Physical Chemistry from Texas A & M University. He then spent two years on a postdoctoral fellowship at the National Research Council in Ottawa followed by one year at the Centre National de Recherche Scientifique in Paris. He joined the analytical department of Shell Research in Amsterdam in 1969 where he has been involved in the development of spectroscopic techniques of analysis.

Dr R E Cohen, BS, MS, is Associate Professor of Chemical Engineering at MIT. His research interests are in the physics and chemistry of polymers with particular emphasis on heterogeneous polymers and filled polymers and their non-isothermal rheology. He has been DuPont Assistant Professor and Esther and Harold Edgerton Assistant Professor at MIT. He is the recipient of the Dreyfus Teacher-Scholar Award for a period of five years beginning in 1977. During 1972-1973 he was ICI Post Doctoral Fellow at Oxford University in the UK.

Dr J van Dongen received his Master's degree in chemistry from the State University of Utrecht, the Netherlands, in 1968. He then joined the Organic chemistry department of this University, where, in 1974, he received his PhD. In the same year he joined Shell Research in Amsterdam, where he has been involved especially in the development of NMR spectroscopy.

Dr E A Flexman graduated with a Bachelors degree in Chemistry from Bradley University in 1962 and a PhD in Organic Chemistry from Indiana University in 1967. He worked as a chemist at the Northern Regional Laboratory, USDA, during the summer of 1962, and was employed as a summer associate in the Central Research Laboratories of the 3M Company during 1964. In 1966, he joined the Plastics Department of the DuPont Company at the Experimental Station Laboratories where he has worked with olefin copolymers, perfluorinated resins, and polyacetals in addition to nylon.

Dr G F Freeguard graduated at University College Swansea in 1957 when he then joined the Atomic Energy Authority. In 1959 he was appointed to the research staff at Liverpool College of Technology and in 1961 he moved to a similar post at the University of Exeter. From 1964 he has been at the University of Nottingham where he is a senior lecturer in the Department of Chemical Engineering.

Dr S Gagg graduated from Illinois Institute of Technology, Chicago in 1974 with a PhD degree in Mechanics. He joined Borg-Warner Chemicals in 1975 as a Senior Research Engineer in Polymer Physics Group.

Dr F Haaf graduated with a degree in chemistry from Technische Hochschule Aachen, Germany, in 1962. After postdoctoral work at Indiana University, USA, he joined the Elastomers Department of Du Pont in Wilmington Delaware in 1964. After returning to Germany in 1968 he worked for BASF on various assignments in the field of plastics research.

Dr D Hardt graduated with a Doctor's degree in Chemistry from Bonn University in 1960. He joined Bayer AG in 1960 to work in the scientific polymer research until 1967. Then he changed to the Application Division for Plasticisers and Additives for thermoplastics. This group he is heading at present.

Dr D L Hunston received his BS and PhD degrees in Physical Chemistry from Kent State University. He then worked for 2 years at Northwestern University on a NIH Postdoctoral Fellowship. Since joining the Naval Research Laboratory in 1971, he has directed his efforts toward understanding the rheological properties of polymeric systems ranging from dilute solutions to highly cross-linked solids.

Mr B Z Jang, BS, is doctoral research assistant in the Chemical Engineering Department at MIT.

Dr R P Kambour received a PhD in Chemistry from the University of New Hampshire in 1960. Since joining General Electric in that year as a member of the research staff he has specialized in polymer physics with particular emphasis on mechanisms of failure in thermoplastics. He is a Fellow of the American Physical Society, a member of the Editorial Advisory Board of Polymer Engineering and Science, and 1968 recipient of the Union Carbide Chemicals Award of the Division of Organic Coatings and Plastics Chemistry of the American Chemical Society.

Mr H Keskkula received his PhD degree from the University of Cincinnati in 1953. He joined The Dow Chemical Company and has worked in the field of styrene polymers. In 1968, he became an Associate Scientist.

Miss S C Kunz graduated with a degree in engineering, summa cum laude, from the University of California, Los Angeles in 1972. After receiving an MS degree in 1974, she joined the Engineering Department at the University of Cambridge to do post-graduate research for a PhD in the field of fracture of reinforced polymers. She is currently a member of the technical staff in the Composites Division at Sandia Laboratories, New Mexico, USA.

Mr S Miller graduated with a Bachelor of Sciences degree in Chemical Engineering in 1970 from Ohio University and a Master of Science in 1972 from Ohio University. He joined the General Electric Company at the Corporate Research and Development Center. In 1975 he transferred to the Major Appliance Laboratories (GE) as a Plastics Developmental Engineer.

Dr H Munstedt got his diploma in physics from the University of Stuttgart, Germany, in 1967 and his doctoral degree from the same university in 1971. After one year as a Leverhulme European visiting fellow at the City University London he joined the BASF company in 1972 where he is the head of a research laboratory for rheology.

Mr J Murphy graduated with an Honours Degree in English from Exeter University, Devon, in 1957 and joined British Cellphane as a copywriter, transferring after a few years to British Resin Products as a Press Officer. In 1964 he joined the new newspaper Plastics and Rubber Weekly as Assistant Editor, becoming Editor in 1969 and later acting as UK/German Coordinator in the 'start-up' of a 'sister' publication in Germany, Kunststoff und Kautschuk Woche. In May last year he set up his own independent Business Newsletter for the plastics industry, entitled 'Plastics Industry Europe'.

Mrs L V Newmann graduated with a First Class Honours Degree in Mechanical Engineering from Imperial College in 1975. She is now studying for her PhD with Professor Williams.

Dr K Nikpur graduated from the Arya Mehra University in Telran and subsequently studied for his PhD under the supervision of Professor Williams at the Imperial College. He is now a Research Assistant with Professor William's group.

Dr W Retting got his diploma in physics from the University of Goettingen, Germany, in 1951 and his doctoral degrees from the University of Bonn in 1956. He joined the Leitz Company at Wetzlar, Germany, in 1957, transferring to BASF in 1960 as head of a research laboratory for the mechanical properties and fracture behaviour of polymers.

Prof G Reiss is Professor of Polymer Chemistry at the Ecole Nationale Supérieure de Chimie de Mulhouse - Université de Haute Alsace and head of the polymer department since 1968. He is Administrator of the French Polymer Group (GFP).

Mr E H Rowe received a BA from Kalamazoo College in 1941 and an MA from the University of Missouri in 1943. He has been employed as a physicist at The BFGoodrich Company in research since 1945. He has had projects requiring the responsibility for electron microscopy, x-ray diffraction; mass spectrometry and other technologies. He is now a Research Associate responsible for materials research for The BFGoodrich Research and Development Center. He has presented and published many papers on the toughening of thermoset resins and composites by the addition of reactive liquid polymers. He is a member of ASTM D-20, D-30, and SPE.

Prof G Scott after graduation with a first class honours degree in Chemistry from Balliol College, Oxford, in 1952, Professor Scott joined the Research Department of ICI Organics Division where he became Manager of the Polymer Auxiliaries Section in 1959. Before being appointed Head of Grangemouth Works Research and Development Department in 1965, he published a book entitled 'Atmospheric Oxidation and Antioxidants' (Elsevier 1965) which was designed to bridge the gap between the scientific and technological aspects of this industrially important subject. Appointed to a Chair of Chemistry at Aston in 1967, Professor Scott strongly advocates a deeper involvement of academics in socially orientated research. In accordance with this principle, his own research activities as Head of the Polymer Research School are concerned with industrial objectives and their broader social implications. Successful outcomes of this research approach have been the development of photodegradable polymers for the packaging and agricultural industries which are now manufactured in several countries and more recently in collaboration with the Rubber Research Institute of Sri Lanka the development of polymer-bound antioxidants for rubber and plastics used in aggressive environments.

Dr N S Sridharan received his MS and PhD degrees from the University of Michigan and his BS degree from IIT, Madras. In 1976-1977 Dr Sridharan was a postdoctoral associate at the Illinois Institute of Technology and is currently employed as a research engineer with Continental Can Company in Chicago, Illinois. Dr Sridharan has published four papers in the area of yielding of glassy polymers.

Dr J Stabenow since 1953 scientific assistant at Fritz-Haber-Institut of Max Planck Gesellschaft Berlin, Germany, graduated with a degree in physics from Freir Universität Berlin in 1959. He joined the BASF Aktiengesellschaft with special responsibility for structural research, especially electron microscopy.

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Dr J B Vander Sande, BE, is Associate Professor of Materials Science and Engineering at MIT where he is in charge of the central microscopy facilities in the Center for Materials Science and Engineering. His research interests are in the quantitative study of microstructure by microscopy and diffraction techniques; and in the study of the structure-property relationship in materials. He was the recipient of a Fulbright-Hays Grant for post doctoral study at Oxford University in the UK during 1970-1971.

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Dr A F Yee graduated with a BS in Chemistry from the University of California, Berkeley, in 1967. In 1971 he obtained a PhD in Chemistry from the same University. From 1971 to date Dr Yee has been employed as Staff Physical Chemist with the General Electric Corporate Research, Schenectady, NY, USA.

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PHASE SEPARATION IN POLYBUTADIENE - POLYSTYRENE SYSTEMS

H. Keskkula*

Several aspects of polybutadiene (PBD) morphology in a polystyrene (PS) matrix have been considered. In quiescent polymerizations of styrene, it has been shown that, at low PBD concentrations, a spontaneous phase inversion occurs and complex rubber particles, typical of those of impact polystyrene, are formed. The effects of PS molecular weight and excessive PBD grafting on the rubber phase stability and morphology have been studied. While low molecular weight PS causes delayed phase inversion, large rubber droplets and poor stability, excessive rubber grafting leads to spontaneous destruction of the typical complex particles.

INTRODUCTION

Rubber modified polystyrenes are prepared by dissolving 5-10% styrene-butadiene copolymer rubbers (SBR) or polybutadienes (PBD) in styrene, followed by the polymerization of this rubber solution to yield a complex toughened heterophase polymer. Because of the incompatibility of polystyrene (PS) and rubbers (1), a phase separation, followed usually by a phase inversion, occurs early in the polymerization. Also, in addition to styrene homopolymerization, grafting of styrene onto rubber occurs, providing the necessary polymeric emulsifier for stabilization of the rubber droplets (2). The formation of these droplets occurs normally only if a sufficient shearing agitation is provided during the critical inversion range, when the volume fractions of the two phases are about equal and the viscosity is still relatively low (3,4). If no shearing agitation is provided, typically it is shown that an interpenetrating PS-rubber network is formed (2).

It is the purpose of this report to examine first the effects of the absence of agitation in systems containing low rubber levels, and excessive rubber grafting. Second, the effects of PS molecular weight and polybutadiene grafting on the rubber phase stability and morphology are examined in this study.

*The Dow Chemical Company, Midland, Michigan, 48640, USA

RESULTS AND DISCUSSION1. Quiescent Polymerization of Polybutadiene in Styrene

An interpenetrating PBD-PS network results from a quiescent styrene polymerization, in the presence of 5% PBD. When reducing the PBD (Diene HD 55) content from 5 to .06%, spontaneous phase inversion and droplet formation take place. With the PBD content below 4%, discontinuities in the interpenetrating polymer network (IPN) are observed and at concentrations below 1% complex rubber particles similar to those of commercial polystyrenes are found. In fact, an evaluation of several PBD-s and SBR-s shows that discontinuity in the IPN occurs at 1-3% rubber level, where styrene is polymerized thermally in the presence of rubber at 120-130°C.

Styrene/butadiene (S/B) block copolymers have been shown to form various morphological, micro-phase-separated forms when dissolved in styrene, followed by polymerization (5,6). Grafted PBD from a commercial IPN, separated by a solvent extraction technique, shows morphological features similar to those resulting with S/B block copolymers (Figure 1).

It is known that rubber grafting is enhanced by peroxide initiation (7,8) and also by such compounds as β -bromostyrene (β bs) (9).

Quiescent styrene polymerizations in the presence of 5% PBD and 0.5% β bs were carried out. From Figure 2, it is apparent that even at low conversion the rubber membrane continuity has been destroyed. Continuing the polymerization to 41% conversion, a total breakdown of rubber into particles below 1000 Å has taken place (Figure 3).

2. Effect of PS Molecular Weight on Rubber Particle Formation

It has been shown that the molecular weight of the rubber plays a significant role in the control of the rubber particle size (4,10,11). With increased solution viscosity, it becomes more difficult to break the rubber phase into small droplets during the critical period after phase inversion. An increased rubber content gives rise to a similar effect (11).

The effect of PS molecular weight on the rubber droplet morphology is more difficult to study directly, because when PS molecular weight is changed, also rubber grafting is usually affected. It appears of importance that the effect of PS molecular weight be studied, at least up to the critical period after phase inversion, since it may be surmised that the viscosity of the PS phase is even more important than that of the rubber phase. After the phase inversion, the lower viscosity PS phase is a continuous phase and therefore, controls shear stress imposed on the system (12).

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In the presence of increasing amounts of chain transfer agents e.g., t-dodecyl mercaptan (tdm) (0.1 to 0.2%), partial polymerization of rubber-styrene solutions give polymeric oil-in-oil (POO) emulsions with decreasing stability. This instability may be due to decreasing viscosity or due to the change in the nature of the graft emulsifier, i.e., molecular weight or amount. It has been shown by Fischer (7) and also in Table 1 that the amount of PBD which is not grafted is somewhat less with a mercaptan in a mass system.

Apparent viscosities of several impact polystyrene (IPS) prepolymers are shown in Figure 4. The dramatic effect of tdm on viscosity and rubber droplet size is clearly evident. A similar effect on viscosity has been reported by Freeguard (13). In all cases, phase inversion had taken place, but with tdm, even at the end of the experiment at 23-27% conversion, rubber droplet size was very large (to 100 μm). Upon high-shear mixing in a Brookfield Counter-Rotating mixer, viscosity was dramatically reduced and rubber droplet size reduced to 1-10 μm . Without tdm, the droplet size was about 1 μm by the end of prepolymerization. It appears from these experiments that the overall viscosity of the prepolymers influences the phase inversion point, as well as droplet morphology significantly. Even though the use of tdm gives rise to a rubber phase which has a higher fraction of graft, the reduced molecular weight of the grafted chains may play a significant role in reducing the POO emulsion stability and affecting droplet size.

Accordingly, it is desirable to use another independent method to study the effects of viscosity and the nature of the POO emulsifier on the stability and the dispersed phase size of these emulsions. Synthetic partial polymers may serve as useful model systems (14). They are prepared by co-dissolving in styrene a rubber, PS and a S/B block copolymer to produce polymers with rubber structure similar to those of IPS-s. The polymerization of these emulsions may be carried out in the absence of shearing agitation. Accordingly, synthetically made POO emulsions of constant composition were prepared with more of the block copolymer emulsifier than normally required and varying only the polystyrene molecular weight.

TABLE 1 - Effect of Additives on PS Molecular Weight and Grafting¹

Additives	Styrene Conversion, %	$\bar{M}_w \times 10^{-3}$	\bar{M}_w/\bar{M}_n	Ungrafted PBD %
None	26.9	298	2.1	69.6
0.2% tdm	24.9	75	1.8	62.0
1% β bs	27.5	113	1.8	28.1

¹ 6% Diene HD55, 7% ethyl benzene, additive as indicated: tdm, t-dodecyl mercaptan; β bs, beta bromostyrene. Isothermal polymerization at 120°C, 60 rpm.

All of the polymers were dissolved in styrene by slowly rotating in a wide-mouth jar on a ball-mill. Rubber droplet size was found to decrease markedly with increasing viscosity of the POO emulsions. Rubber droplets in excess of 50 μm diameter were found with PS-19 and the lower molecular weight polystyrenes. With PS-40 and 60, all droplets were below 10 μm . It was also observed that the POO emulsions made with relatively low molecular weight polystyrene demixed readily, while there was no indication of demixing of the high viscosity emulsions. The data are summarized in Table 2.

TABLE 2 - Characteristics of Synthetically Made Prepolymers

Polystyrene	$\bar{M}_w \times 10^{-3}$	Artificial Prepolymer ¹	
		Apparent visc., -Pa.s, at 19.6 sec ⁻¹ 25°C,	Stability after 1600 hours
PS-4	60	.7	unstable ($\psi=0.4$) ³
PS-14	205	4.8	unstable ($\psi=0.1$) ³
PS-19	284	13.6	stable
PS-40	354	25.6	stable
PS-60	432	37.2	stable

¹ Composition: 6.7% Diene CF-35, 24.0% polystyrene, .9% styrene-butadiene (60/40) block copolymer (20% in ethylbenzene, $\eta_{\text{inh}} = 1.32$), 64.7% styrene, trace benzoquinone.

² Determined by Haake-Rotovisco.

³ ψ = volume ratio of upper to lower layer in the demixed solution.

3. Effect of Excessive Rubber Grafting on Particle Morphology

Polystyrene grafted rubbers and S/B block copolymers have been established as POO emulsifiers in PS-PBD systems (2,14). The nature of these, however, has been relatively little studied in relationship to the final rubber particle morphology (18).

In this work, PBD was grafted in a thermally initiated polymerization of styrene and with the addition of beta bromostyrene (βbs) (9), which increases styrene grafting onto polybutadiene.

A mixture of MEK/acetone was used with partial polymers to separate free polystyrene from rubber and graft as described earlier (15). Graft and PBD were separated similarly by first dispersing the mixture in benzene/methylene chloride to which n-octane was added to separate PBD. This procedure was repeated to effect a complete separation. The purity of PS and PBD fractions was checked by refractive index. Based on these data, graft distribution was determined according to the random grafting model proposed by Tung and Wiley (16).

Table 1 summarized the data on the effect of t-dodecyl mercaptan and beta bromostyrene on the extent of grafting and PS molecular weight of partial styrene polymers. It is apparent that β bs acts as a graft promoter as well as a modest chain transfer agent; tdm does not influence significantly the percent of PBD grafted, but is a stronger chain transfer agent. PS and graft molecular weight are sufficiently high that these grafts should be satisfactory P00 emulsifiers. Data similar to those in Table 1 were obtained in quiescent polymerizations and also in experiments with n-dodecyl mercaptan. In case of thermal polymerization ($\sim 30\%$ conversion) without additives, about 20% of the PBD has one graft, while with 1% β bs, multiple grafted PBD accounts for about 50% (10% without graft promoters).

Figure 3 shows PBD morphology from a quiescent polymerization of 5% PBD solution in styrene, containing 0.5% β bs. A rubber phase comprising discrete small particles is noted, quite unlike the IPN-s obtained in the absence of graft promoting β bs. Polymerization with shearing agitation causes the beginning of the destruction of expected rubber particles (Figure 5) at rather low β bs levels of 0.2%.

It may be concluded that, with the increasing extent of grafting, smaller particles may be obtained at first, but ultimately a disintegration of the rubber phase particles into spherical, rod or complex layered structures occurs.

With a mercaptan modifier, causing a large change in viscosity, but not significantly affecting the % rubber grafted, the result is rather different. The internal structure of the particles remains similar to those of commercial IPS-s, only the size and stability are adversely affected.

Based on the experiments described in this study, Figure 6 shows some generalizations of the rubber particle formation in a styrene-PBD system. When polymerization conditions are used, where relatively low graft level is achieved (e.g., thermally initiated polymerization) increasing shearing beyond the critical shear rate (17) gives rise to reduced particle size. These particles contain typical PS occlusions. When higher grafting levels are obtained, typical rubber particles with occlusions may not be obtained at all. In this case, rubber membranes with sufficient graft concentration will form specific microphase-separated morphological shapes, determined by the ratio and molecular weight of PS and PBD segments in the graft molecule (6).